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THE NATURAL REMOVAL OF LEAD POLLUTANTS FROM A SUBURBAN ATMOSPHERE

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Patrick R. Atkins
and
Paul Kruger, Program Director

Federal Water Pollution Control Administration
Training Grant WP-009
and
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STANFORD UNIVERSITY

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The results of a study to determine how effectively natural cleansing processes remove lead pollutants in the atmosphere are presented. The study included (1) field smapling in Palo Alto, California, to determine the effectiveness of sedimentation, impaction, rainout, and washout, and (2) a laboratory study to determine how well specific lead compound aerosol particles act as nuclie for droplet formation. The field sampling data indicated that sedimentation is responsible for a major portion of the lead removal in the Palo Alto area.

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Department of Civil Engineering
Stanford University
Stanford, California

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The growing volume of high speed, high density traffic in urban and suburban areas, and the increasing use of alkyl lead antiknock fluids in gasoline produce increasing amounts of lead contamination in populated areas. Lead pollutants now account for more than 3% of the mass of all airborne particulate matter over some cities. City-wide monthly average concentrations in excess of four micrograms of lead per cubic meter of air have been reported and lead concentrations in excess of 50 micrograms of lead per cubic meter of air have been observed near major roadways. The lead combustion products from automobiles are exhausted predominantly in the form of submicronic sized particles which can be absorbed through the respiratory tract of humans. Recent studies have shown that a correlation exists between exposure to atmospheric lead contamination and the resulting concentration in blood and tissue.

Since no regulations to control lead pollutants at the source are expected in the foreseeable future, this study was undertaken to determine how well lead pollutants are removed by natural cleansing processes after being injected into the atmosphere. A field sampling program was conducted in Palo Alto, California, a San Francisco suburb, to determine

the effectiveness of sedimentation, impaction, rainout and washout in removing lead contaminants from the atmosphere. It was suspected that the nucleation of water on the submicronic lead particles might be an important process contributing to the removal of the lead pollutants. Therefore, a laboratory study was conducted simultaneously to determine how well specific lead compound aerosol particles act as nuclei for droplet formation. A modified thermal-gradient diffusion chamber was used to produce slightly supersaturated conditions similar to a growing cloud.

The field sampling data indicate that sedimentation is responsible for a major portion of the lead removal which occurs in the Palo Alto area. More than ninety percent of the lead pollutants reaching the surface during the one-year sampling period were collected in dry fallout. Approximately one percent of the total dry fallout collected near a major expressway was lead. A correlation was found between the lead particulate matter and total dustfall in the dry fallout samples. The limited rainfall (approximately 13 inches per year which occurs only during the late fall and winter months) accounted for five to ten percent of the lead removal at the sampling sites. Lead concentrations in excess of one milligram per liter were found in some rainfall samples, and average concentrations of 0.18 and 0.04 milligrams per liter were observed near the freeway and at the outskirts of the city, respectively.

Sedimentation and rainfall scavaging are relatively inefficient processes for the removal of submicronic particles. A growth process must occur to make the lead particles susceptible to these cleansing processes. The field data suggest that the formation of water droplets around the lead particles may account for the rapid removal of lead pollutants. The nucleation studies show that lead compound particles may act as nuclei for droplet formation, even at low supersaturations. The results of these studies indicate that the thermodynamic approach using accepted values of solubility, wettability and heat and vapor diffusion, fails to adequately describe the nucleation process. Relatively insoluble PbI_2 crystals appear to make better nuclei than very soluble $Pb(NO_3)_2$ crystals. Parameters such as the crystalline structure and surface free energy may be very important in determining how well a particle will act as a condensation nucleus. Future studies with the thermal-gradient diffusion chamber may assist in better describing the nucleation process and in determining why certain particles seem to make better condensation nuclei than others.

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CHAPTER ONE

INTRODUCTION

Environmental pollution is one of the most detrimental by-products of our current level of technological achievement and economic prosperity. The environmental conditions in and around most urban centers show evidences of the thousands of tons of waste products generated each day. The industrial and domestic wastes discharged into the waterways, the gaseous and particulate wastes injected into the atmosphere, and the huge volume of solid wastes produced daily present urgent problems. The removal, and ultimate disposal, of these wastes should be accomplished quickly and efficiently to prevent disease, property damage and nuisance conditions.

Until the early 1950's the problem of atmospheric pollution had received almost no consideration in the popular press, and little scientific study because the enormous assimilative capacity of the atmosphere made extensive pollution appear impossible. A few decades ago the atmosphere was considered to be an unlimited reservoir for waste disposal; but the heavily industrialized and densely populated urban complexes which exist today have demonstrated that this is not the case. Damage to buildings, personal property, crops and livestock resulting from air pollution has been estimated to exceed 11 billion dollars annually in the United States (Gustavson, 1958). The cost of the damage to human health resulting from air pollution cannot be evaluated in dollars. No significant data are available on the number and type of diseases which can be attributed to air pollution, but it appears that the rate of respiratory related diseases is increasing in heavily polluted areas. Severe air pollution has been blamed for deaths in several instances: New York City in 1966, London, England in 1962 and 1952, and Donora, Pennsylvania in 1948. Therefore, there is a pressing need to learn more about atmospheric pollution and to develop methods to prevent this contamination.

The problems associated with air pollution and its control are varied, complex and deeply interrelated. It is difficult to study any single facet of the problem without becoming involved with broad overlapping segments. Likewise, the results obtained from a study dealing with a specific contaminant may be applicable to a wide range of similar contaminants. The purpose of this report is to present the results of a study of the natural processes by which a particular type of airborne particulate matter is removed from the atmosphere. The specific pollutant considered in this work is lead particulate matter, but the results obtained may be applicable to other metal and non-metal pollutants which are injected into the atmosphere as particulate matter.

Lead is a minor constituent of the total pollution load of the atmosphere, but a potentially dangerous one. It is wide-spread and can be accurately detected in low concentrations. The major source of lead pollution in urban areas is the automobile. Alkyl lead compounds are added to gasoline to increase the octane rating of the fuel and thus reduce the tendency for the engine to knock. Lead compounds are exhausted from the engine in the form of small inorganic particles (many below one micron in diameter) which may remain airborne for considerable periods of time and travel great distances. This lead is distributed throughout the environment and contaminants the air, land, and surface waters. Thus, these lead compounds can be ingested by humans through air, water or food. Many different opinions concerning the severity of the problem of lead pollution have been published in the past. For example, Kehoe (1958) reported that the available data indicate no danger presently exists from lead pollution, while Patterson (1965) believed that the average resident of the United States was being subjected to severe lead insult.

No federal standards for the control of lead pollution from automobiles have been seriously considered and no devices are yet available to significantly reduce the amount of lead exhausted by automobiles (Gilbert, 1959). Our present political and economic climate indicates that, until conclusive evidence of danger to the public is provided, leaded gasoline will continue to be used at an increasing rate in the future, possibly subjecting the general population to an increased level of lead pollution. Since it does not appear likely that lead pollution will be controlled at the source, this study of the natural processes by which lead pollutants may be removed after being injected into the atmosphere was undertaken. Perhaps certain types of lead compounds may be more efficiently removed under natural conditions and thus present less of a pollution problem. The results of studies of this type may lead others to a search for specific additives which, when combined with leaded gasoline, will cause the lead combustion products to be exhausted predominantly in a form for optimum removal from the atmosphere.

The natural processes which may be important for removing lead and other particulates from the atmosphere include:

(1) Sedimentation: which occurs when a particle is large enough to overcome the lifting forces of convective and wind currents.

(2) Impaction: which occurs when the inertial forces on a particle are great enough to overcome the aerodynamic drag which keeps it in the airstream. The particle will then cross the stream lines as they bend around a surface and collide with that surface.

(3) Washout: which occurs when a falling raindrop collides with an airborne particle too large to move around the drop. This scavaging process occurs below clouds.

(4) Rainout: which occurs when particulate matter is present in the supersaturated environment of a growing cloud. The small particles may act as nuclei for the formation of small droplets and thus be incorporated into growing raindrops. This nucleation process may also occur on particulate matter present below cloud level, producing droplets large enough to be affected by sedimentation, impaction and washout.

All of these processes are effective to various extents depending upon atmospheric conditions and the nature of the contaminant. However, nucleation appears to be one of the more important mechanisms contributing to the removal of submicronic-size lead compound particles. Without this growth process, such particles would not be removed effectively by sedimentation or rainfall.

This study has been conducted in two phases:

a) a laboratory phase in which the dry uniform aerosols of various lead compounds were studied to determine how effectively the different particles acted as condensation nuclei under controlled conditions similar to those occurring in the atmosphere; and

b) a field study phase in which the effectiveness of the various removal processes was determined for the bulk lead contaminants in the atmosphere.

Though the two approaches are quite different, the results obtained from both phases of this program are complimentary and will be presented in this report.

CHAPTER TWO

BACKGROUND INFORMATION

The scientific literature contains a considerable amount of information concerning lead contamination and aerosol technology. However, the results of many investigations concerning the lead content of the atmosphere and the resulting public health implications present a somewhat confused picture. Most investigators agree that lead contamination exists, but the levels of contamination and the dangers associated with it are still uncertain. Several researchers using different methods have reported considerably different analytical results and have often drawn contradictory conclusions concerning the sources of lead pollution, atmospheric concentrations, lead aerosol size distribution, lead content of human blood tissue, and the effects of lead on animals and people. The behavior of lead particulate matter and other aerosol particles under natural atmospheric conditions is not well understood. However, some information pertinent to this study is available and is summarized in this chapter.

Sources of Lead Pollution

Lead and lead compounds are used in practically every type of industry. A few of the major uses for lead in the United States include:

Storage batteries, solder (for electrical connections, automobile construction, and food containers), paints, alloys, ammunition, type metal, insecticides, and anti-knock fluids for gasoline (Working Group on Lead Contamination, 1965). Industrial lead consumption increases each year and the trend has been pronounced in the last few decades, largely due to the automobile industry. For example, in 1954, 2190 million pounds of lead were used and in 1964 the amount had risen to 2404 million pounds annually (Stokinger, 1965). During this period, the amount of lead added to domestic gasoline increased from 320 million pounds to 448 million pounds, accounting for 60% of the increase.

Several independent studies, using different analytical techniques, including particle size distribution (Robinson, 1963), and isotope concentration (Chow, 1965), indicated that the lead added to gasoline and exhausted from automobiles is the major source of lead pollution in many areas. Atmospheric lead pollution resulting from industrial plants processing lead and its products can be quite severe in local areas, but the overall contribution by such sources to the pollution load of large areas is minimal (California Department of Public Health, 1967). Burning of lead-bearing materials in open dumps (autobodies, construction equipment, domestic trash, etc.) can result in the emission of lead due to the low melting points of some lead compounds. However, samples taken of the effluent from subterranean burning in a

New Orleans dump contained low lead concentrations which indicate that this is not a significant source of lead pollution (McCalden, 1965). Cholak (1961) reported that the burning of coal should produce an appreciable amount of lead pollution and that the degree of contamination should decrease as the amount of coal burning decreased. However, Robinson (1966) and McCalden (1965) discounted coal as a significant source of lead pollution, even in such cities as Cincinnati, where over 12,000 tons of coal are burned daily.

Lead is added to gasoline in the form of alkyl compounds to improve the octane rating of the fuel and thus reduce knocking in engines (Advisory Committee on Tetraethyl Lead, 1959). The amount of anti-knock fluid added varies with the fuel blend and the octane rating desired, but the maximum used presently is equivalent to 4.23 grams of lead per gallon (Working Group on Lead Contamination, 1965). This maximum limit is agreed upon by the private companies involved and, as yet, is not regulated by federal law. However, the federal government is consulted before the maximum limits are set by the companies. The last increase in the maximum lead concentration in gasoline was approved in 1962 when the level was raised from 3.18 grams of lead per gallon. The average amount of lead present in all gasoline sold in the United States is slightly more than two grams per gallon, but as the demand for higher octane gasoline increases, this average value may also increase (Working Group on Lead Contamination, 1965).

When leaded gasoline is burned in an engine, the alkyl lead compounds decompose at the high temperatures and pressures developed by the combustion process and form lead oxides. These oxides inhibit chain reactions which would otherwise form volatile compounds and result in secondary detonations or knocking (Working Group on Lead Contamination, 1965). The decomposition products then react with the scavengers (ethylene dibromide and ethylene dichloride) that are added to reduce the accumulation of solids on the critical areas of the combustion chamber. Studies by Hirschler et al. (1957) indicated that 70 to 80% of the lead in gasoline is eventually exhausted into the atmosphere over 20,000 to 30,000 miles of city and highway driving. An average automobile travelling at 60 miles per hour will burn approximately one gallon of gasoline every 15 minutes (Panel on Electrically Powered Vehicles, 1967). Since gasoline contains an average of two grams of lead per gallon, 1.4 to 1.6 grams of lead particulate matter will be exhausted during a 15 minute period. Thus, approximately 1.75 milligrams of lead pollutants will be produced each second, or 20 micrograms of lead will be produced during each foot of travel.

Hirschler et al. (1957), from a chassis dynamometer study, and Tufts (1959) reported that the lead aerosols from automobile exhausts contain a large number of particles greater than one micron in diameter; but, Mueller et al. (1964) and Pries (1957) reported that lead aerosols from automobiles consist primarily of submicronic particles. In a recent study, Robinson et al. (1963) found, using a modified Goetz Aerosol Spectrometer, that almost all of the lead emitted by automobiles is contained in particles less than one micron in size, and that these particles can remain airborne for long periods of time. The mass median equivalent diameter (for unit density spheres) was found to be 0.25 microns with 75% of the mass contained in particles less than 0.45 microns in diameter.

Extent of Lead Pollution

The extent of lead contamination resulting from our massive use of lead is surprising. Studies reported by Gould (1966) of the traces of lead pollution trapped in the Greenland polar ice indicate an alarming increase in atmospheric lead in the last decade, even in very remote areas. A study by Schroeder and Balessa (1961) of tree rings also showed an increase in lead content in recent decades. The amount of lead introduced into our relatively small urban environments each year was reported to be more than 100 times greater than the amount of natural lead leached from soils by streams and carried to the oceans over the entire earth (Chow et al., 1962). Tatsumoto and Patterson (1966) reported that there are indications that about nine-tenths of the lead in the upper mixed zones of the open oceans originates from mined lead, and Murozumi et al. (1965) stated that the atmosphere of the northern hemisphere contains about 1000 times more than natural amounts of lead.

Patterson suggested that there are several striking differences between natural and existing lead states. He estimated natural rates of lead intake and natural body burdens from data reported by others and concluded:

1. Existing average body burdens of lead are about 100 times larger than natural burdens;
2. Existing rates of average lead absorption are about 30 times higher than natural rates;
3. Under existing conditions, atmospheric sources of lead make highly significant contributions to absorbed lead, while such sources make insignificant contributions under natural conditions.

This last statement is illustrated by Table I which shows that airborne lead makes a significant contribution to the total amount of lead absorbed by urban dwellers. The fifth column of this table indicates the relative importance of the various routes by which lead can enter the body. Since respiratory absorption is very efficient for small particulate matter (40% of the lead ingested is absorbed), airborne lead is of particular importance. A person living in an urban area

TABLE 2-1

INGESTION AND ABSORPTION OF LEAD BY MAN
(Patterson, 1965)

Substance	Intake/Day	Pb Conc.	Pb Ingested (μg/day)	Fraction Absorbed	Pb Absorbed (μg/day)
Food	2 kg	0.2 ppm	400	0.05	20
Water	1 kg	0.01 ppm	10	0.1	1
Urban Air	20 m^3	1.3 $\mu g/m^3$	26	0.4	10
Rural Air	20 m^3	0.05 $\mu g/m^3$	1	0.4	0.4
Tobacco Smoke	30 cigarettes	0.8 μg/ cigarette	24	0.4	10

with an average airborne concentration of 1.3 micrograms of lead per cubic meter of air ($\mu g/m^3$) will absorb 50% more lead than a person living in a rural area. Studies conducted in several cities (Working Group on Lead Contamination, 1965) showed that the average lead levels often exceeded 1.3 $\mu g/m^3$ for long periods of time. During the Fall and Winter of 1961 the average lead concentrations found in three cities were: Cincinnati, 2.4 $\mu g/m^3$; Philadelphia, 3.8 $\mu g/m^3$; and Los Angeles, 4.1 $\mu g/m^3$. A person living in Los Angeles during this period would have absorbed 225% more lead than a rural dweller. Near a source of pollution, the lead concentration of the atmosphere can be several times greater than these average values. Goldsmith et al. (1967) found a dose-response relationship for lead in blood and tissue. Studies by the Working Group on Lead Contamination (1965) also indicated that a correlation exists between the blood lead concentration of humans and the amount of time they spend in an atmosphere containing a high concentration of lead pollutants, such as a city center or near a busy freeway. Similar studies by Thomas et al. (1967) in Los Angeles showed that people living very near a freeway had significantly higher blood lead concentrations than people living near the coast in a relatively unpolluted part of the city.

Effects of Lead Pollution

Patterson recently stated that his evidence suggests, clearly and strongly, that the average resident of the United States is being subjected to severe "chronic lead insult" (1965). Kehoe (1964) has long maintained that the evidence available to him demonstrated conclusively that the contribution made by tetraethyl-lead contamination of the atmosphere to the total absorption of lead by the American population has been remarkably small in either relative or absolute terms and that it has been minute physiologically and insignificant hygenically, despite the tremendous increase in the use of tetraethyl-lead. Gusev (1962) reported that experimental evidence from studies with animals indicated that pathologic and histologic changes of the brain and spinal cord together with functional shifts in the higher nervous activity are induced by exposures to atmospheric lead concentrations corresponding to those now experienced by people living in many large cities. Hardy (1967), Cantarow et al. (1944) and Bell (1924) all reported that exposure of mothers to lead has a damaging effect upon fertility, the course of pregnancy, and the development of the fetus. Children appear to be especially susceptible to the effects of lead poisoning; growing cells seem to be affected more severely than adult cells, especially soft tissue cells, according to Byers (1943). Therefore, early brain damage can result if children are exposed to high lead contamination.

The maximal atmospheric lead levels currently observed have been too low to produce clinical evidence of lead poisoning in humans, but the existing standards now considered as safe levels for lead concentrations in air are related to industrial exposures for adults and do not take into account long-term effects, responses of persons with impaired renal or other organic functions, or possible childhood susceptibility (Motor Vehicles, Air Pollution and Health, 1962). The limit that can be tolerated may be reached quickly or may have been surpassed already in some areas, and yet no controls on lead pollution exist and little effort is being made to reduce lead contamination.

Aerosol Technology

To study the removal of lead particulate matter from the atmosphere, an understanding of some of the properties of aerosols (solutions of droplets or particles in a gas) is required. Aerosols are usually classified into three categories according to size. Particles with a radius less than 0.1 micron are called Aitken nuclei; between 0.1 and 1.0 microns they are called large nuclei and above one micron they are called giant nuclei. The Aitken nuclei are by far the most numerous, but the large and giant nuclei are the most active in cloud, fog and raindrop formation.

Particles larger than five to ten microns do not remain a part of the atmospheric aerosol since they settle out rapidly. Extremely small aerosol particles (< .001 micron) tend to coagulate rapidly to form particles which are less mobile and more resistent to further coagulation. Fletcher (1962) derived an approximate equation to predict the rate at which the concentration, n, of particles of radius, r, will decrease in a relatively uniform aerosol. With r in centimeters, n in particles per cubic centimeter, and t the time in hours, his expression reduces to

$$-\frac{1}{n}\frac{dn}{dt} = 10^{-6}\, n \left(1 + \frac{10^{-5}}{r}\right)$$

For $r = 0.005$ micron and $n = 10^5/cm^3$ (a typical value in urban air), the time required for the particle concentration to decrease by one-half due to coagulation is approximately 30 minutes. For $r = 0.1$ micron and $n = 10^3/cm^3$ (also typical of urban air), the time required for a 50% reduction in concentration is more than 500 hours. Thus, the size distribution of large and giant nuclei is not significantly affected by coagulation, but the size distribution of the Aitken nuclei ($r < 0.1$ micron) is constantly being modified by this process.

The presence of atmospheric aerosols has long been recognized and much has been published on this subject. Aitken (1923) began studying the size distribution of atmospheric particles before the turn of the century and developed instruments and techniques to count the small aerosol particles. His studies were primarily conducted at large water vapor supersaturations, where all the particles present were active as condensation nuclei.

Early studies of the activity of atmospheric nuclei at small water vapor supersaturations, comparable to those occurring in the atmosphere, were conducted by Wieland (1956) using a thermal gradient supersaturation chamber. The number of nuclei present which formed droplets at various degrees of supersaturation was deduced by counting the craters formed by the droplets as they fell into a varnish layer at the bottom of the chamber. He found that the total number of nuclei active at supersaturations below 1% was in the range of 50 - 1000 cm^{-3}, which is typical of cloud droplet concentration, even though the total number of aerosol particles present in the atmosphere is much higher (Twomey, 1959). Squires (1965) has also used a similar instrument to determine the variation in the number of active nuclei with height above the earth's surface.

Why some particles are more active than others as condensation nuclei is not fully understood. Fletcher (1962) and others have developed equations to predict which types of particles will be active nuclei at given degrees of supersaturation. These equations are based on classical thermodynamic considerations assuming that certain parameters used to describe macroscopic processes are equally valid for microscopic processes. The parameters include solubility, wettability, heat and vapor diffusion rates, surface tension, and vapor pressure.

In general, these equations suggest that large hydroscopic or soluble particles will be activated first in a growing cloud. Hicks (1966) has examined Fletcher's analysis for soluble particles and developed an approximate equation for the fractional supersaturation, s, required to activate the nuclei with the given characteristics. The resulting expression is

$$s = 4.86 \times 10^{-8} \left(T^3 d^3 \frac{i\rho}{M} \right)^{1/2}$$

where

T = temperature

d = particle diameter

i = van Hoff's dissociation factor

ρ = density of the particle

M = gram molecular weight

Using typical values for atmospheric dust particles of $M = 200$ grams per mole, $\rho = 4$ grams per cubic centimeter (g/cm^3) and $i = 2$, the above equation indicates that a supersaturation of 0.2% is sufficient to nucleate all the soluble particles present with a diameter greater than 0.1 microns. However, Fletcher determined that much higher supersaturations are required to bring about the nucleation of insoluble particles which exhibit a finite contact angle. For example, a particle, one micron in diameter, would require a supersaturation in excess of 25% before it could act as a nucleus for raindrop formation, if it consisted of a compound that exhibited a 36° contact angle for water.

Junge (1963) used a different approach in his analysis of the interaction between aerosol particles and rainfall. He related the concentration, k, of the constituent in the cloud water (mg/l) to the physical characteristics of the cloud and pollutant by the equation

$$k = c \frac{\varepsilon}{L}$$

where

c = concentration of the constituent in the cloud ($\mu g/m^3$)

ε = collection efficiency

L = total amount of water condensed in cloud air (g/m^3).

From this relationship, ε may be estimated for various aerosols. However, there are no significant data published upon which to base meaningful calculations, so Junge has not yet determined the collection efficiency for any given aerosol.

Airborne particulate matter may be so active as condensation nuclei that all available moisture in the atmosphere is trapped on small particles and rainfall is prevented. Thomas (Los Angeles Air Pollution Control District Report, 1967) and Schaefer (Cowen, 1968) reported that the heavy particulate loading of the atmosphere around New York City may have contributed to the extended dry period which prevailed over the Northeastern United States recently, but no supporting data has been produced as yet. Twomey (1959) also suggested that a large aerosol population could have such an effect.

The Removal of Aerosols

Mason (1961) stated that the removal of aerosols is possible by fallout under gravity, impaction of particles on obstacles on the earth's surface, and precipitation processes. The precipitation processes considered are:

1. The consumption of condensation nuclei during the formation of cloud elements;
2. The subsequent attachment of aerosol particles to the cloud elements as a result of Brownian motion;
3. The attachment of aerosol particles to cloud elements due to forces caused by vapor pressure gradients;
4. The collection of aerosol particles by falling raindrops.

A close examination will reveal that many of the removal processes listed are not efficient for submicronic particulate matter.

Sedimentation is an ineffective removal process for small particles. Particles larger than 20 microns radius remain airborne for only a limited time, and their occurrence is therefore restricted to the vicinity of their source. Particles less than one micron in diameter have fall velocities of less than one-tenth of a centimeter per second, thus allowing them to remain airborne for long periods of time.

Impaction of submicronic particles on tree leaf surfaces is possible at normal wind speeds (Byers, 1957). Pine needles and similarly shaped surfaces appear to be aerodynamically attractive for the impaction of particulate matter (Junge, 1961). Thus, trees near a surface source of particulate pollution may increase the rate at which lead aerosols are removed from the atmosphere.

Brownian motion has little effect on particles larger than 0.01 micron (Mason, 1961). The fractional rate of removal of particles of radius r_p and concentration n_p by cloud droplets of radius r_c and concentration n_c is

$$-\frac{1}{n_p}\frac{dn_p}{dt} = C\left[\frac{1 + Al/r_p}{r_p} + \frac{1 + Al/r_c}{r_c}\right](r_p + r_c)n_c = kn_c$$

where c is a constant involving the absolute temperature, and the viscosity of air, and Al represents the Cunningham correction to Stokes' Law (9×10^{-6} cm at STP). Solving

$$n_p(T) = n_p(0)e^{-kn_c t}$$

The half-life of this reaction, i.e., the time required for the concentration of particles to fall by one-half, is

$$t_{1/2} = \frac{0.693}{kn_c}$$

If $r_c = 10$ microns and $n_c = 100/\text{cm}^3$, then

$$r_p = 0.01\ \mu; \quad 0.1\ \mu; \quad 1.0\ \mu$$

$$t_{1/2} = 2.6\ \text{hrs.}; \quad 140\ \text{hrs.}; \quad 2000\ \text{hrs.}$$

Thus, only particles with $r < 0.01$ micron are effectively removed by Brownian capture on cloud droplets within a few hours.

Vapor pressure gradients could effect small particles in a growing cloud, according to Facy (1955). He suggested a mechanism by which small particles in the diffusion field of a growing droplet would be impelled toward the droplet by a force resulting from unequal bombardment on opposite sides by water vapor molecules in the vapor concentration gradient. A satisfactory theoretical treatment allowing assessment of the efficiency of such a mechanism of particle capture has not yet appeared. Goldsmith (Mason, 1961) conducted some experiments with an expansion chamber. He allowed water droplets of several microns radius to grow in the presence of radioactive particles of approximately 0.1 microns radius, and his results indicated that the collection efficiency under these conditions is low.

Aerosol particles may also enter rainfall by colliding with falling droplets. Engleman et al. (1966) recently made measurements of the washout coefficients for several aerosols. During a period of relatively steady rainfall, a known amount of aerosol was injected into the atmosphere from a tower and the rainfall passing through the plume was collected in strategically located buckets. To date, the data are insufficient to report definitive results, but the authors intimated, and others have reported (Mason, 1957; Hocking, 1959), that the effectiveness of raindrop washout of submicronic particles below clouds is very low, even for intense rainfall.

Mason (1961) suggested an equation to determine the rate at which particles of radius r and concentration n(r) below the cloud level will be removed by the scavaging of raindrops of radius R falling at a velocity v. The expression is:

$$dm/dt = \pi R^2 v \sum^{r} E(R, r) n(r) 4/3 \rho r^3 \pi$$

where dm/dt is the rate of mass accretion of aerosols, E(R, r) is the collection efficiency of raindrops for a particle, and ρ is the particle density. Some values of E calculated for an air pressure of 900 millibars (mb) and temperature of $0^{\circ}C$ are given in Table 2-2. The particles are assumed to be spherical and of unit density. Similar results have been reported by Langmuir (1948), Hocking (1958), and Pearcey and Hill (1957). Some data have been reported by Turner (1955) to support these conclusions.

TABLE 2-2

COLLECTION EFFICIENCY OF PARTICLES OF RADIUS r BY FALLING DROPS OF RADIUS R

(Mason, 1961)

R(mm)	r(μ)					
	1	2	4	6	8	10
0.1	0.01	0.03	0.18	0.47	0.67	0.83
0.6	0.01	0.17	0.54	0.74	0.85	0.91
1.0	0.01	0.15	0.52	0.74	0.83	0.90
1.8	0	0.08	0.45	0.68	0.80	0.86
3.0	0	0.02	0.33	0.55	0.71	0.81

Nucleation and the growth of water droplets around atmospheric nuclei are extremely important phenomena. The change of phase required for the formation of liquid droplets in a vapor medium cannot occur under natural cloud conditions without condensation nuclei (Fletcher, 1962). In an environment completely free of all solid particles, supersaturations on the order of 400% are required for droplets to form. The supersaturations normally achieved in a growing cloud seldom exceed 1% (Junge, 1963), so all raindrops that are formed must have atmospheric aerosol particles as nuclei. Therefore, a large number of aerosol particles should be removed by nucleation during a rainstorm. This process is called rainout for obvious reasons. As stated earlier, thermodynamic considerations have lead to general equations which predict how well and at what rate certain particles will act as condensation nuclei, but the mechanisms involved are not completely understood. The number of small nuclei observed in cloud and fog droplets (Junge, 1963) indicates that rainout may be an effective removal process for atmospheric aerosols similar to the lead compound products exhausted by automobiles.

Therefore, it appears that the major processes active in the removal of submicronic lead particulate matter are impaction of the particles on obstacles on the earth's surface, and rainout of the particles which act as condensation nuclei. The other processes mentioned are only effective for particles of much larger or smaller size than the lead aerosols under consideration. However, several of the processes may act in such a combination as to effect a significant removal of the lead particles from the atmosphere.

The mechanisms occurring in the atmosphere are extremely complex and intricately interconnected; no simple theory is capable of explaining these phenomena. We can only hope to arrive at good approximations which will reasonably define the processes.

CHAPTER THREE

THEORETICAL CONSIDERATIONS

Recent studies have shown that the lead aerosol particles exhausted by automobiles are small enough in size to remain airborne for long periods of time. However, Cholak (1961) and Patterson (1965) have reported that a considerable amount of lead contamination has been detected on city streets and in soil and on crops grown near major roadways. Hirschler et al. (1957) estimated that approximately 50% of the lead pollutants exhausted into the atmosphere are removed rapidly. In the absence of rainfall, the lead particulate matter must be removed from the atmosphere by turbulent transfer from air to the surface, by impaction on surfaces, or by sedimentation. Sheppard (1958) reported that turbulent transfer in the surface sub-layer could occur if the pollutants were in the form of gases or extremely small particles. However the turbulent transfer of lead particulate matter will be very low since the diffusion coefficient for particles greater than 10^{-6} cm becomes extremely small. A portion of the lead contamination, especially that found on plants, may result from impaction of the small particles on exposed surfaces, but the amounts found in soil and dustfall samples suggests that sedimentation accounts for much of the rapid removal.

The fall velocity (i.e., settling rate in still air) v, of small particles, $< 50\ \mu$ radius, can be determined from Stokes' Law:

$$v = 2/9\ \frac{r^2 \rho}{\eta}\ g$$

where

r = particle radius

ρ = particle density

η = kinematic viscosity of air

g = acceleration due to gravity

Under normal atmospheric conditions, when $g = 980$ cm/sec^2, $\eta = 182.7 \times 10^{-6}$ g/cm sec., $v = 1.3 \times 10^{6}\ \rho\ r^2$.

Assuming $\rho = 4$ g/cm^3 for a typical lead compound aerosol particle, it can be shown that particles less than $1.4\ \mu$ in radius will have a fall velocity of less than 0.1 cm/sec and will not be significantly affected by gravity. Normal convective and wind currents near the surface will be sufficient to keep such particles airborne. Fleagle et al. (1963) reported that most particles less than $20\ \mu$ in radius would be unaffected by sedimentation. Therefore, a rapid growth process must occur near the roadway to account for the excessive pollution of the land surface by lead particulate matter from automobiles.

Coagulation of the small aerosol particles cannot account for the larger particles required to explain the sedimentation. Junge (1963) reported that coagulation of airborne particles greater than 0.1 micron was inefficient and that coagulation would not produce a significant change in the size distribution of an aerosol consisting of particles ranging in size from 0.05 to 5 microns in diameter, even after several hours. However, it does appear likely that the nucleation of water on lead aerosol particles and a rapid growth of water droplets by condensation could occur and account for the increased lead contamination near a roadway.

Nucleation is the inception of a stable droplet in a pre-existing gaseous system. An energy barrier must be overcome before nucleation can take place. Each water molecule which changes from the vapor phase to the liquid phase releases energy (evidenced by the heat of condensation), but energy is required to form the surface of the growing droplet (surface tension). The energy relationship which governs nucleation can be expressed in simplified form by

$$\Delta G = n(\mu_L - \mu_V)V + \sigma A$$

where

ΔG = net change in free energy

n = number of molecules per unit volume of droplet

μ_L = free energy of a liquid molecule

μ_V = free energy of a vapor molecule

V = volume of embryo droplet $(4/3\ \pi\ r^3)$

A = surface area of embryo droplet $(\pi\ r^2)$

σ = interfacial free energy per unit area of droplet

Since μ_V is larger than μ_L (gaseous phase is a higher energy state), the first term will be negative. As the embryo droplets become larger, the negative term, proportional to the radius cubed, will increase faster than the positive second term, which is proportional to the radius squared. Therefore, an increase in the number of molecules changing phase will decrease the free energy change. When an increase in the number of molecules changing phase produces a negative free energy change, a stable droplet will result. An increase in the number of molecules in the entire system, i.e., an increase in the supersaturation, will increase the probability of a stable droplet forming. Likewise, the introduction of a particle in the system, which can attract and hold vapor molecules, will increase the supersaturation locally and may result in the formation of a stable droplet. In the latter case, a portion of the surface energy of the nucleus particle may contribute to the energy required to form the liquid-vapor interface of the droplet--thus lowering the energy barrier somewhat. Theoretical calculations and experiments conducted in expansion cloud chambers have shown that relative humidities in excess of 400% are required for nucleation to occur when no nuclei are available (Fletcher, 1961). Relative humidities of less than 100.5% are required for nucleation to occur if suitable nuclei are present (Hicks, 1966). Since the supersaturation required to form droplets is much lower if nuclei are present, all droplets which form in the atmosphere grow around condensation nuclei, which are normally present in excess.

Approximately one gram of water vapor is produced for each gram of gasoline consumed (Amelin, 1967), and this vapor is present in the exhaust gases from automobiles. When the hot gases cool in the exhaust system and in the atmosphere, local supersaturations result and water droplets can form. In this supersaturated environment, lead particles, which make up as much as 40% of the total particulate matter in the exhaust stream (Mueller et al., 1964), may act as nuclei for droplet formation. The droplets which are produced will begin to evaporate when the supersaturation is reduced by dilution and mixing, but in a humid atmosphere they may remain large for several minutes. During this time the large droplets will undergo rapid mixing due to the turbulence caused by the traffic. This will allow the droplets to come into contact with many large dust or combustion product particles present near the roadway, increasing the opportunity for coagulation to occur. The efficiency of this coagulation depends on many factors--the temperature difference between the exhaust gas and the atmosphere, the size distribution and number of dust and lead aerosol particles present, wind conditions, the relative humidity of the atmosphere, and traffic conditions, i.e., average vehicle speed, traffic density, and number of lanes of traffic.

Nucleation and droplet growth may also be important in removing the lead pollutants which reach higher levels of the atmosphere. The increasing amounts of lead contained in the precipitation collected in remote "unpolluted" areas, i.e., Greenland, are evidence of the fact that lead contaminants which are small enough to remain airborne for extended periods can enter into rainfall. Such small particles (below one micron in size) are not removed in significant amounts by rainfall scavaging because of their mobility which allows them to follow an air streamline around a falling drop instead of colliding with the drop. Therefore, such lead compound particles probably enter the rainfall at the cloud level by acting as nuclei for droplet formation.

Very little is known about differences between aerosol particles of the same size which might make one more effective as a nucleus than another (Fleagle et al., 1963). Nor is it known to what extent interaction of particles is important. In a mixed particle population such as exists in the atmosphere, the particles present compete with one another to act as nuclei for droplet formation. Equations predicting nucleation rates based on thermodynamic concepts and accepted values of wettability, solubility and diffusion rates do not agree well with experimental results. Little difference was observed recently between the nucleating behavior of non-wettable paraffine aerosols and aerosols made of very wettable substances (Weickmann, 1968). In the region very near the nuclei surface, the classical concepts evidently do not apply. Weickmann suggested that, in this region, due to kinetic gas effects, classical concepts of heat and vapor diffusion might not hold. The ability of a particle to attract water vapor and thus increase the supersaturation very near the particle surface may be more important. The surface energy and surface structure of the potential nucleus are factors to consider. Speaking on the subject of the heterogeneous nucleation of ice crystals, Byers (1966) reported that there are indications that the process (ice crystal formation) operates after a thin film of water has been absorbed on the surface of the nucleus. The film forms ice as a result of nucleation by the particle surface, but the film is so thin--about 100 Å--that droplets are not normally detected and the ice crystal forms as if from the vapor. He further stated that PbI and AgI are good ice nuclei. Both compounds are insoluble and exhibit large contact angles for water; yet, nucleation on the particle surfaces evidently occurs before the compounds can produce ice crystals.

Reliable instruments, such as the well known Aitken, Scholz and Nolan-Pollak counters, have been widely used to determine condensation nuclei concentrations in many areas and under different conditions. The principal of operation of these counters is similar and they differ mostly in mechanical arrangement and method of counting the nuclei. The air sample to be investigated is drawn into a chamber saturated by contact with moist cloth, blotting paper or porous ceramic material. When equilibrium has been reached, the sample is expanded quickly in a nearly adiabatic manner to produce a supersaturated environment. However, small expansions result in rapid and large supersaturations which are very different from the conditions which normally occur in the atmosphere. Many particles which may be active as condensation nuclei in these expansion counters may not be active in atmospheric condensation. Therefore, these counters cannot be used to study the nucleation process as it occurs in nature.

Recent investigations by Wieland (1956) were performed using a thermal gradient diffusion chamber to produce small supersaturations (0.1% to 1%). The conditions produced in such a chamber are more like natural atmospheric conditions than those obtained by expansion counters. The nucleation which occurs in a chamber of this type should be similar to atmospheric nucleation. Squires (1966) has also used a modified thermal gradient chamber to study airborne condensation nuclei concentrations.

The thermal gradient supersaturation chamber utilizes the nonlinear relationship which exists between the saturation vapor pressure and temperature of an air mass. The chamber consists of a closed vessel with a warm top surface and a cooler bottom surface. Water vapor is provided by means of a moist absorbent cloth covering the top surface and a water reservoir covering a portion of the bottom surface. This enables both heat and water vapor to be distributed throughout the chamber by diffusion. Both heat and water vapor diffuse according to the classical heat equation:

$$\frac{\partial T}{\partial t} = D_H \frac{\partial^2 T}{\partial x^2} \quad \text{and} \quad \frac{\partial P}{\partial t} = D_V \frac{\partial^2 P}{\partial x^2}$$

where D_H and D_V are the diffusion coefficients for heat and water vapor, respectively. D_V is slightly larger than D_H for the temperature range of this study.

If left undisturbed, a linear water vapor and temperature gradient will develop across the chamber. The temperature halfway between the top surface and bottom surface will be

$$T_{1/2} = \frac{T_B + T_T}{2}$$

and the corresponding vapor pressure will be

$$P_{1/2} = \frac{P_B + P_T}{2}$$

Figure 3-1 illustrates the nonlinear relationship which exists between the temperature and saturation vapor pressure of an air parcel (solid line) and the linear relationship which will exist in the chamber. As the figure illustrates, when the bottom surface temperature is 10° and the top surface temperature is 20°, $P_{1/2} = P_{15}* =$ 12.80 mm Hg. However, at $T_{1/2} = 15^{\circ}$, the saturation vapor pressure for air, P_{15}, is 12.80 mm Hg. Therefore, the air near the center of the chamber will be supersaturated with respect to water vapor. The maximum supersaturation for a ten degree temperature difference, S_{10}, will be

$$S_{10} = \frac{P_{15}*}{P_{15}} = \frac{13.35}{12.80} = 1.042$$

If air is injected into the chamber at a constant rate to simulate the dynamic conditions in a growing cloud, mixing takes place in the chamber and the linear gradients across the chamber disappear. Thin

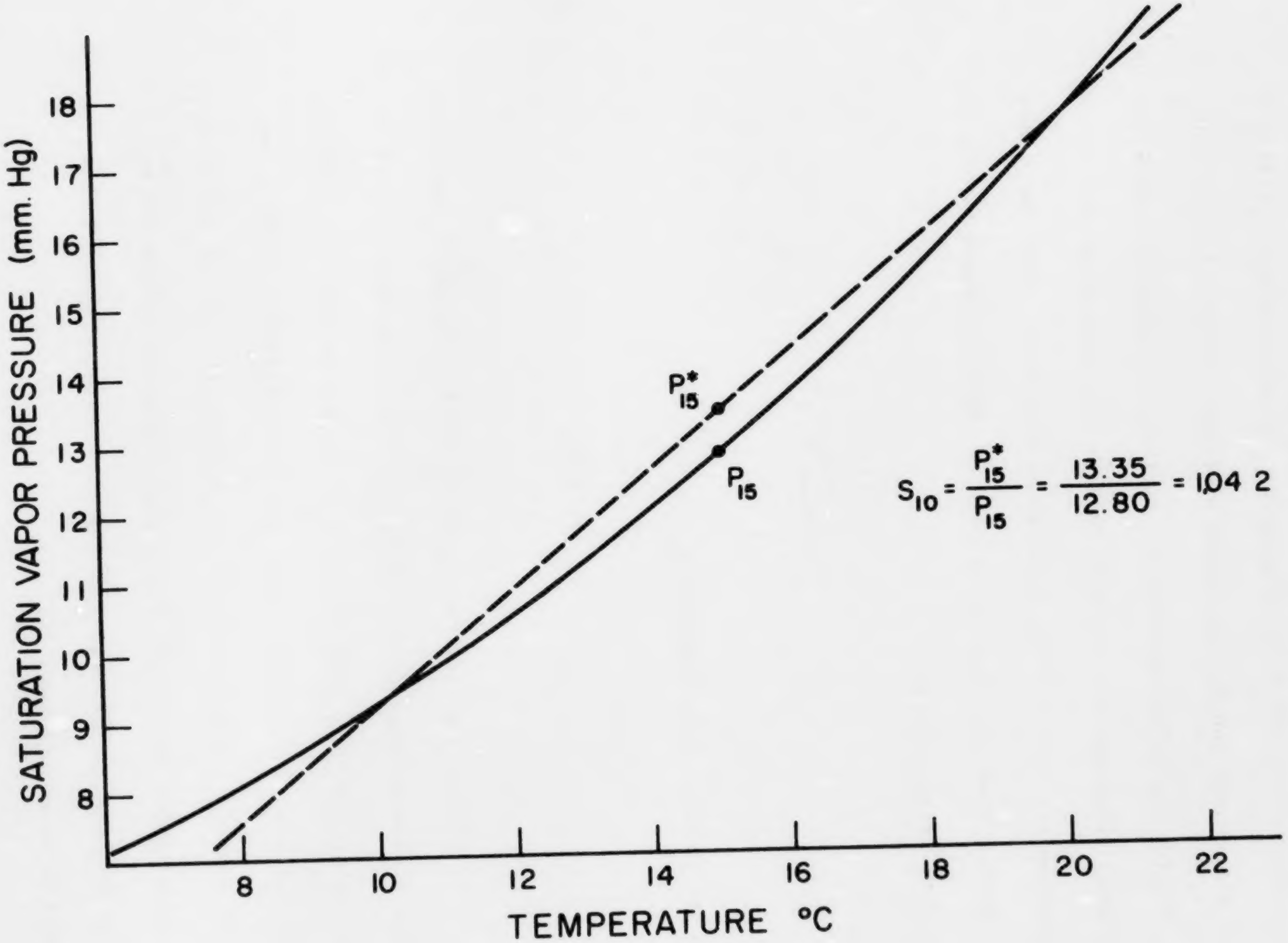

FIGURE 3-1
SUPERSATURATION VAPOR PRESSURE IN AIR (SOLID LINE) AND VAPOR PRESSURE PROFILE
IN THE DIFFUSION CHAMBER (DASHED LINE)

boundary layers with sharp temperature and vapor pressure gradients are set up near the top and bottom surfaces. Since the conditions at the top and bottom surfaces are similar, the boundary layers will be of equal thickness, and diffusion through both boundaries will be approximately equal, if the temperature difference across the chamber is small. Thus, the vapor pressure, $\bar{P}$, that will exist between the boundary layers will be

$$\bar{P} = \frac{P_T + P_B}{2}$$

and the corresponding temperature, $\bar{T}$, will be

$$\bar{T} = \frac{T_T + T_B}{2}$$

The maximum supersaturation determined for the static case when linear gradients existed, will exist throughout the major portion of the chamber, not just near the center. The higher diffusion coefficient for water vapor ensures that the supersaturation can be maintained even when small amounts of heat diffuse through the air mass. The relationship between the temperature difference of the top and bottom surfaces and the degree of supersaturation produced in the chamber is shown in Figure 3-2.

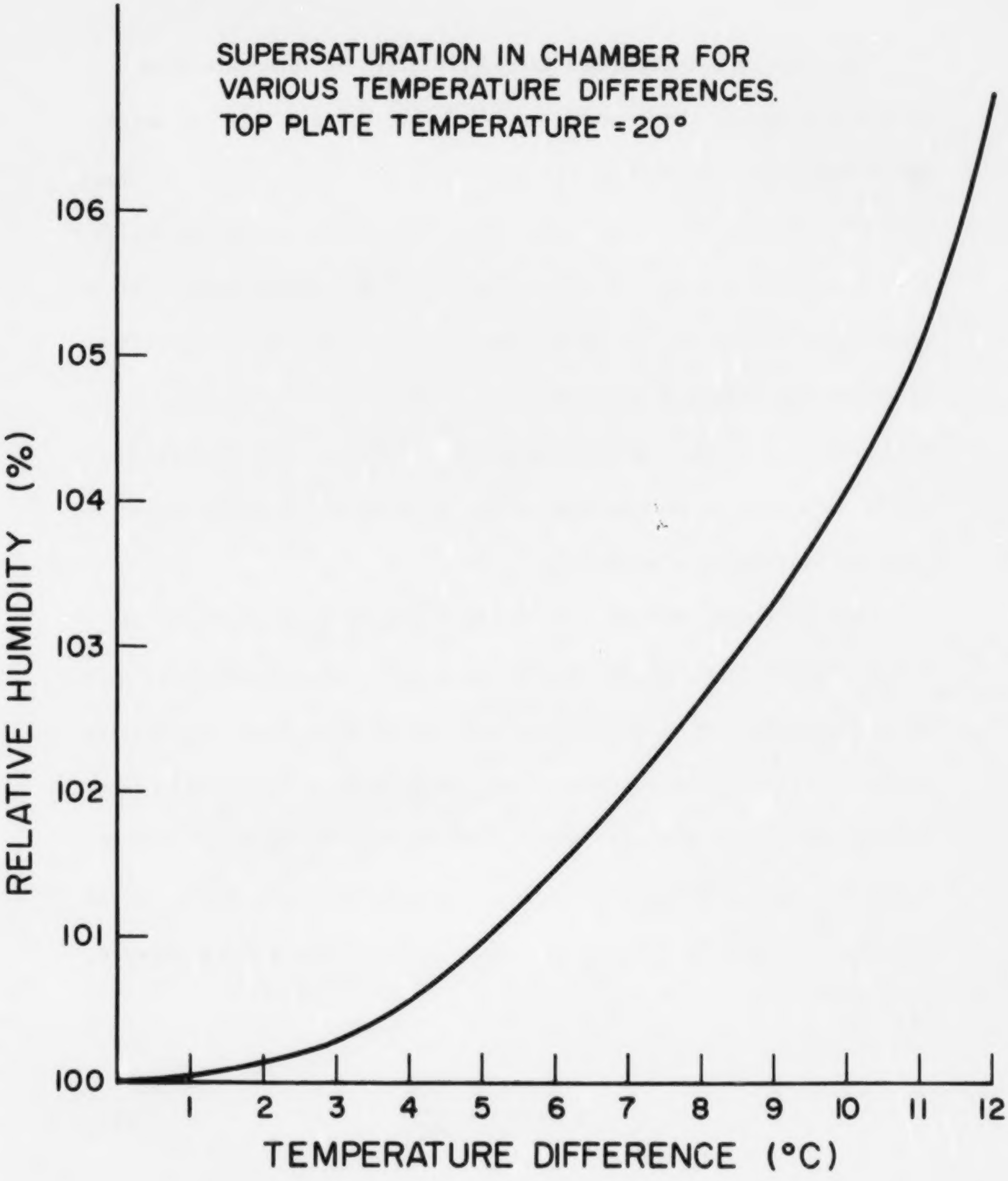

FIGURE 3-2
CALCULATED SUPERSATURATIONS (AS RELATIVE HUMIDITY)
PRODUCED IN THE DIFFUSION CHAMBER

As aerosol particles are introduced into the supersaturated environment inside the chamber, nucleation will occur. If the aerosol number density is kept high, the nucleation of a large number of droplets will deplete the excess water vapor around the aerosol particles, thus reducing the degree of supersaturation. More water vapor will be supplied by diffusion, but if the rate of nucleation on the particles is rapid, the degree of supersaturation may continue to decrease. This reduction in the supersaturation in the area of the droplets will result in a halt in further nucleation and some of the newly formed droplets will begin to evaporate.

Kelvin (1870) deduced that the equilibrium vapor pressure over a curved surface increases as the radius of curvature increases, so that, in an environment where the supersaturation is decreasing, the smaller droplets will begin to evaporate first, and larger droplets will continue to grow, utilizing the water vapor escaping from the smaller. Kelvin's classical formula in terms of equilibrium vapor pressure over a curved surface, p, and the equilibrium vapor pressure over a plane surface, p_o, is:

$$\ln (p/p_o) = \frac{2\sigma}{nkTr} \qquad (3\text{-}1)$$

where

σ = the interfacial free energy of the droplet-air surface (surface tension)

n = the number of molecules per unit volume of liquid

k = Boltzmann's constant

This tendency to evaporate is offset somewhat, i.e., the equilibrium vapor pressure is lowered somewhat, if the nucleus is soluble. Raoult's law states the vapor pressure over a solution decreases as the mole fraction of water in the solution decreases. For a dilute solution, this can be written as:

$$p'/p_o = 1 - \frac{n''}{n'} \qquad (3\text{-}2)$$

where

p' = the equilibrium vapor pressure over a solution

p_o = the equilibrium vapor pressure over pure water

n'' = the number of molecules of solute per unit volume

n' = the number of molecules of water per unit volume

For a spherical droplet

$$n' = \frac{(4/3\pi r^3 \rho' - m)}{M_o} N$$

and

$$n'' = \frac{im}{M_s} N$$

where

r = droplet radius

ρ' = density of solution

m = mass of solute in droplet

M_o = gram molecular weight of water

M_s = gram molecular weight of solute

N = Avogadro's number

i = Van't Hoff dissociation factor

Thus,

$$p'/p = 1 - \frac{3iM_o m}{(4\pi r^3 \rho' - m)M} \qquad (3\text{-}3)$$

For small values of x,

$$e^x \cong 1 + x$$

and, assuming m much smaller than the mass of water in the droplet, the Kelvin and Raoult equations can be combined to yield

$$p''/p_o = 1 + \frac{2\sigma}{nkTr} - \frac{3iM_o m}{4\pi r^3 \rho M} = 1 + \frac{3.3 \times 10^{-5}}{T}\frac{1}{r} - \frac{4.3im}{M}\frac{1}{r^3} \qquad (3\text{-}4)$$

where p'' = equilibrium vapor pressure over a solution droplet. For relatively insoluble lead nuclei, the third term will be small and can be neglected. The growth of the droplets is thus limited by

$$p''/p = 1 + \frac{3.3 \times 10^{-5}}{T}\frac{1}{r} \qquad (3\text{-}5)$$

As the supersaturation is reduced to lower and lower values of p'' by nucleation and growth, the equilibrium value of r will increase. Any droplet smaller than this equilibrium value will begin to evaporate. Eventually an equilibrium value of p'' will be reached where diffusion from the chamber surfaces and evaporation of the smaller droplets will be great enough to supply water vapor at a rate adequate to satisfy the growing droplets.

However, when the large droplets have grown to 15 - 25 microns in size, they will be removed from the system by sedimentation, thus allowing the supersaturation to again increase around the aerosol particles. This increase in water vapor will initiate the nucleation process again and the cycle will repeat itself, producing more large droplets which will precipitate from the system.

The number of nuclei present, the initial supersaturation, and the rate at which nucleation occurs will control the number of droplets reaching the critical size before depletion of the water vapor halts further nucleation. If nucleation occurs at a relatively slow rate, diffusion of water vapor toward the growing droplets and diffusion of heat (heat of condensation) away from the droplets will act to maintain the supersaturation for a relatively long period of time, resulting in the nucleation and growth beyond the critical size of a large number of droplets. If, however, nucleation occurs at a much faster rate, the available moisture will be utilized quickly and a rapid build-up of heat near the droplets will occur. These factors will act to reduce the supersaturation quickly, thus limiting the number of droplets which will reach the critical size. Therefore, an aerosol composed of particles with a slow rate of nucleation will produce a large number of large droplets in the chamber while a similar aerosol composed of particles with a more rapid nucleation rate will produce fewer large droplets.

The growth of droplets which have exceeded the critical size is relatively independent of the composition or nucleating rate of the nucleus. They will essentially act as pure water droplets obeying the Maxwell equation (Amelin, 1967)

$$\frac{dm}{dt} = 4\pi \frac{r^2 D}{R_w T} \frac{dP}{dx} \qquad (3\text{-}6)$$

where

dm/dt = the change in mass of the droplet with time

r^2 = the droplet radius

D = the diffusion coefficient for water vapor

R_w = the universal gas constant

T = temperature near the droplet

dP/dx = the vapor pressure gradient near the droplet

An approximate solution to this equation yields

$$\frac{dm}{dt} = 4\pi \frac{rD}{R_w T} (p_c - p'') \qquad (3\text{-}7)$$

where

p_c = vapor pressure far away from the droplet

p'' = equilibrium vapor pressure over droplet surface

For small droplets, diffusion and heating effects and surface curvature will affect the growth rate, but after the droplet reaches approximately one micron in diameter, these affects are small and equation (3-7) holds. The droplets continue to grow until they are removed by precipitation or until their rate of growth exceeds the rate of diffusion of water vapor from the diffusion surfaces in the chamber. Eventually all large droplets will precipitate to the bottom surface or will be removed in the exhaust from the chamber.

CHAPTER FOUR

EXPERIMENTAL PROCEDURES

The experimental program for studying the atmospheric cleansing processes affecting lead aerosols was divided into a field sampling project and a laboratory study. The sampling project was conducted to observe lead pollutants under natural atmospheric conditions. The laboratory program was conducted to study the reactions of specific lead aerosol particles under controlled conditions closely approximating a growing cloud. Many of the procedures used in this experimental program were developed or modified especially for this work and will be described in some detail.

Field Study Phase

1. Location

The field study was conducted in Palo Alto, California, a suburban city of 56,000 located at the southern end of San Francisco Bay, thirty-three miles from the city of San Francisco. This location has several features which make it ideal for an environmental pollution study of this type.

1. The topography of the area results in a nearly constant wind direction over the city. The high hills on both sides of

San Francisco Bay, and the Bay itself, tend to channel the winds so that they blow from the northwest quadrant approximately 70% of the time (U. S. Weather Bureau, 1967, 1968).

2. Palo Alto and the neighboring cities have a large commuting population. This results in large, but predictable, daily variations in the traffic density in the area.
3. The only major freeway in Palo Alto is the Bayshore Freeway, located on the northern edge of the city. This freeway acts as a source for lead pollutants. The winds bring relatively clean air down San Francisco Bay and across the Freeway, picking up the lead pollutants and carrying them across the city.

The field study was conducted to observe the surface distribution of lead aerosol pollutants in a suburban area, and to determine the effectiveness of sedimentation, impaction, rainout and washout in removing these pollutants. To accomplish these aims, three sampling sites were established and periodic samples of air, dry fallout, and rainfall were taken and analyzed for lead content.

One site was located between the Bayshore Freeway and the freeway frontage road near Colorado Avenue in Palo Alto. The air sampling equipment was located fifteen feet from the closest lane of the six-lane roadway, one foot above pavement level. The dry fallout and rainfall collectors were located 50 feet from the nearest lane. A second dry fallout collector was placed under an 18 foot oleander tree 40 feet from the freeway to collect the drippings from the leaves during periods of rainfall. These drippings contained much of the particulate matter that impacted on the leaf surfaces.

The second site was located in a residential area of Palo Alto, 2.4 miles south of the freeway. The air sampler and fallout and rainfall collectors were placed in an open area near the corner of California and Williams Street.

The third collection site was located 5.1 miles south of the freeway in an open area behind the Stanford campus. The air sampler and the rainfall and dry fallout collectors were placed in a small fenced-in area in the center of a pasture used for grazing cattle.

2. Equipment

The air samplers used in this study were Staplex high-volume samplers, Model TFIA, manufactured by the Staplex Company.[1] The samplers could be used with either four inch circular filter paper disks or 8" x 10" filter sheets. Whatman #41 filter paper was used to collect the lead aerosols. The samplers were capable of drawing air through the 8" x 10" filter sheets at the rate of 65 cubic feet per minute. These high volumes made it possible to use short sampling times of five minutes or less so that variations in lead content over short time intervals could be detected. The Whatman #41 filter paper has been found to have good collection efficiency for submicronic-sized particles, especially at face velocities of one meter per second or greater (Paltridge, 1967). The face velocities achieved in these collections exceeded 2.5 meters per second. The actual efficiencies were checked using Whatman #42 paper, an extremely fine pore paper produced especially for filtering small particles. The Whatman #41 paper collected at least 90% as much lead as was collected by the #42 paper in simultaneous tests. These data are contained in Table 4-1.

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[1] The Staplex Company, 777 Fifth Avenue, Brooklyn, New York.

Polyethylene pans, one foot by one foot by five inches deep, were used to collect the dry fallout at the three stations. Care was taken to place the collectors in an open area, so that buildings, trees and other obstructions would not bias the samples. A site was considered clear if a line drawn from the collector at an angle of 30° to the horizontal did not intersect an obstruction in any direction. The bottom of each collector was kept wet at all times with a layer of distilled water to retain any particles which fell into the collectors. The collector used to catch the drippings from the tree at the freeway sampling site was also a one foot by one foot by five inch polyethylene pan, similar to the fallout collectors.

TABLE 4-1

WHATMAN FILTER PAPER COMPARISON
August 1, 1967

Time (PST)	Filter Paper	Flow Rate (cfm)	Lead Concentration ($\mu g/m^3$)	#41 Concentration / #42 Concentration
0545	#41	65	4.84	0.95
	#42	22	5.10	
0615	#41	65	6.15	0.93
	#42	22	6.62	
0645	#41	65	10.5	0.99
	#42	22	10.6	
0715	#41	65	2.40	1.26
	#42	23	1.90	
0755	#41	65	10.3	0.98
	#42	22	10.4	
0820	#41	65	11.7	0.88
	#42	24	13.3	
0905	#41	65	6.70	0.79
	#42	22	8.50	
1005	#41	65	6.40	0.97
	#42	23	6.60	

Two types of rainfall collectors were used in this study. The collector at the freeway site was a 12 inch diameter polyethylene funnel with a six inch vertical lip to reduce splash losses. The base of the funnel was threaded and a four liter polyethylene bottle was attached to collect the rainwater. The collectors at the other two sites were 13.5 inch diameter polyethylene buckets, ten inches deep. The collectors were placed in stands so that they were three feet above the ground surface. The rainfall samplers were near the fallout samplers at the three sites in open areas that would not be affected by surface obstructions.

Sampling and Analytical Procedures

1. Air Samples

Immediately after each air sample was taken, the filter paper was removed from the sampler and sealed in an envelope. In the laboratory, the filter papers were quartered and two quarters were prepared for independent lead analysis. The other two quarters were stored in the envelopes for future analysis, if necessary. The quarter samples were prepared by digesting them for several hours in 6 N HNO_3 to ash the filter paper and release the particulate material. The lead analysis used is explained in detail in a subsequent section. If the results of the independent tests differed by more than 5%, the third and fourth sections of the filter paper were analyzed. However, in almost all cases, the one quarter sheet tests agreed well, indicating that the lead particulate matter was uniformly distributed over the filter surface.

Air samples were also taken to determine the total amount of particulate matter present in the atmosphere. Whatman #41 four inch disks were used. The disks were first dried at 103°C for three hours, cooled in a dessicator and weighed to the nearest one-tenth of a milligram. They were then enclosed in polyethylene bags for transport to the sampling site. Large air samples were filtered through these disks to collect a significant amount of particulate matter. The sampling time ranged from one to twenty-four hours, depending upon the estimated pollution loading of the atmosphere. At the laboratory, the filter disks were again dried, cooled and weighed to determine the weight of particulate matter collected. No attempt was made to determine the non-volatile fraction, since the filter disks used were not suitable for dry ashing.

2. Rainfall and Fallout Samples

The fallout material in the polyethylene pans was collected each week by transferring the water in each pan to sixteen ounce polyethylene bags, scrubbing the collector surfaces with a soft brush to dislodge any remaining particles, and rinsing these particles into the collection bag with a portion of the sample water. Distilled water was then added to cover the bottom surface. The collectors were left open during periods of rainfall and the contribution of lead pollutants attributed to the rainfall was subtracted from the total amount collected.

In the laboratory, the volume of each sample was determined and aliquots were taken for the following analyses:

1. Total and non-volatile solids.--A 50 milliliter aliquot was added to a porcelain evaporating dish of known weight and evaporated to dryness at 103°C. The dish was cooled in a dessicator and reweighed to determine the weight of the total solids present. Next, the dish was placed in a 600°C muffel furnace for ten minutes, cooled and reweighed to determine the weight of the non-volatile (inorganic) solids present.
2. Total and non-volatile suspended solids.--Whatman GF/C glass fiber filter pads were used to remove the particulate matter from the samples. The glass fiber pads are capable of retaining very fine particles. They are constructed of borosilicate fibers less than one micron in diameter, and are approximately 200 microns thick. This construction produces relatively long meandering pathways through the filter which trap the particulate matter. Unlike membrane filters, the

GF/C pads do not have a uniform pore size. Large particles could possibly pass through the larger pathways. However, several comparison tests made with GF/C pads and Gelman type 00 Metrical filters (0.45 micron pore size) indicated that the glass pads were as efficient as the Gelman filters in removing the lead particulate matter from the samples. Therefore, the total and non-volatile suspended solids analysis was conducted by filtering a 50 milliliter aliquot of each fallout sample through a pre-weighed 4.25 centimeter diameter Whatman GF/C pad using a millipore filter apparatus. After the aliquots were filtered, the pads were dried at 103°C for three hours, cooled in a dessicator and reweighed to determine the weight of the suspended solids present. Next, the pads were placed in a 600°C muffel furnace for ten minutes, cooled and reweighed to determine the weight of the non-volatile (inorganic) suspended solids present. Two blank pads were subjected to the same procedure each week to detect any weight loss in the pads from the heating steps. A constant loss of 0.9 milligrams was observed when the pads were heated in the 600° oven for ten minutes.

3. Soluble lead.--The 50 milliliter aliquots of filtrate from each suspended solids analysis were collected in 125 milliliter

flasks and analyzed for lead content. For this study, all lead contained in the filtered aliquots was considered to be soluble.

4. Total lead.--An aliquot of the unfiltered sample was placed in an 125 milliliter erlynmeyer flask and analyzed for total lead. The size of the aliquot depended upon the location from which the sample was taken--normally 5 milliliters for the freeway samples, 10 milliliters for the residential samples, and 25 milliliters for the foothill samples.

The rainfall collectors were scrubbed with a soft brush and rinsed with distilled water shortly before or soon after each rainfall began. Samples were then taken during the storm and soon after its termination to minimize evaporation losses. The rainfall samples were collected in polyethylene bags and transported to the laboratory for analysis. A 50 milliliter aliquot was filtered through a GF/C glass fiber filter pad, collected in an 125 milliliter flask and analyzed for lead content. This lead was assumed to be soluble. A second 50 milliliter aliquot was placed directly into an 125 milliliter flask and analyzed for total lead.

The drippings from the tree at the freeway site were also collected during and after each rainfall. Each sample was collected in polyethylene bags and transported to the laboratory. The same procedures as mentioned above were followed to analyze the sample for total solids, non-volatile solids, total lead and soluble lead. However, much smaller aliquots were required. A 25 milliliter aliquot was used for the solids analysis, a five milliliter aliquot was used for the soluble lead analysis, and a one to five milliliter aliquot was used for the total lead analysis.

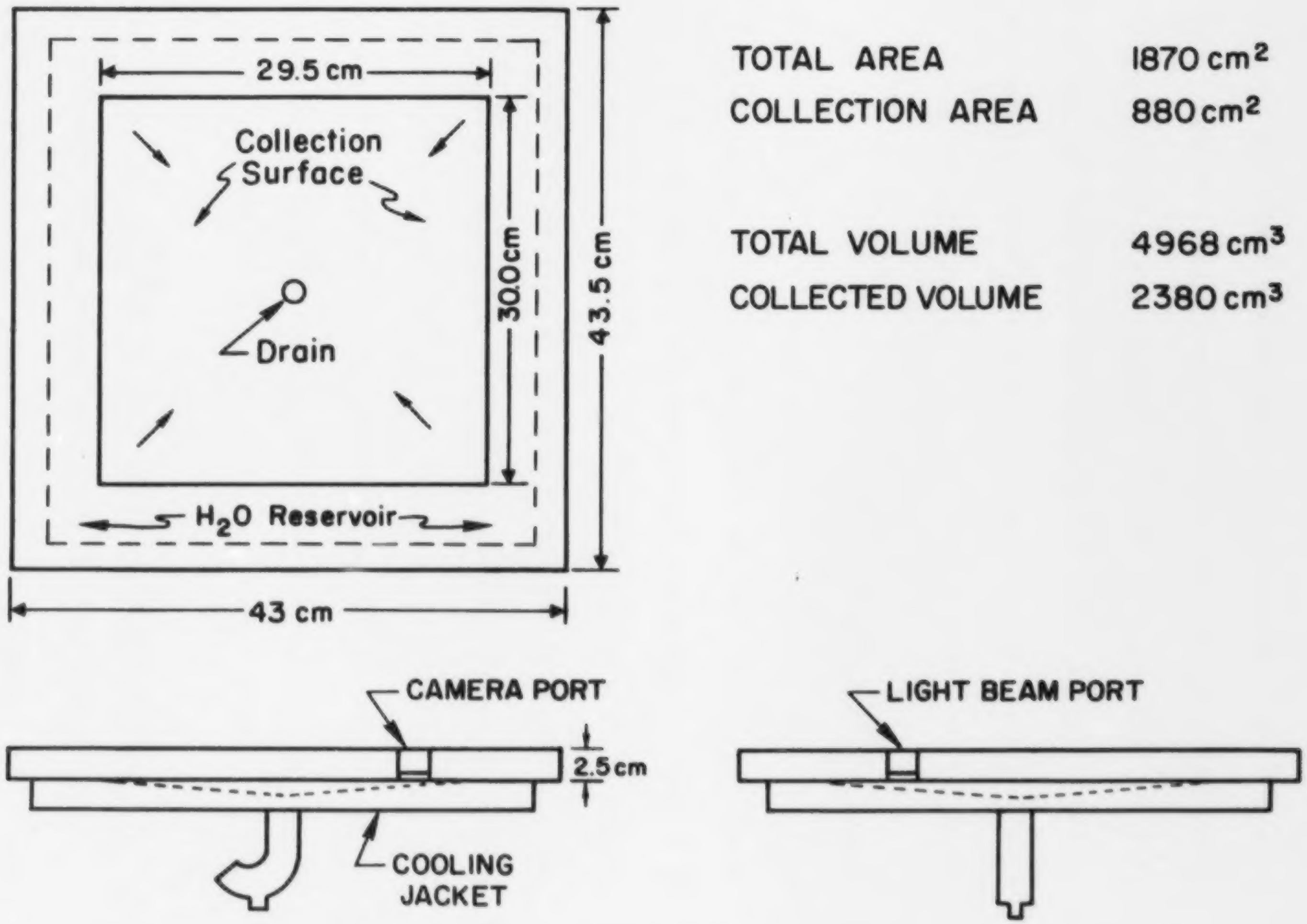
Laboratory Study Phase

In order to study the nucleation process in the laboratory, a thermal gradient diffusion chamber was used to simulate natural atmospheric conditions. The chamber was designed to produce water vapor supersaturations in the range of 0.1% to 4%. Since it would be extremely difficult to obtain lead aerosol particles from automobile exhaust in a known concentration and particle size distribution, lead compound aerosols were prepared in the laboratory and injected into the chamber. The results of the nucleation tests were used to draw generalized conclusions which may be applicable to many atmospheric nuclei.

1. The Diffusion Chamber

The thermal gradient diffusion chamber was constructed of plexiglas. The dimensions are shown in Figure 4-1. A length-to-height ratio of 20 was used to provide large diffusion surfaces and minimize the effects of the side walls. The bottom surface was divided into

THERMAL GRADIENT SUPERSATURATION CHAMBER


29.5 cm
Collection Surface
Drain
30.0 cm
43.5 cm
H_2O Reservoir
43 cm
CAMERA PORT
2.5 cm
COOLING JACKET
LIGHT BEAM PORT

TOTAL AREA	1870 cm^2
COLLECTION AREA	880 cm^2
TOTAL VOLUME	4968 cm^3
COLLECTED VOLUME	2380 cm^3

FIGURE 4-1

two sections, a smooth collection surface and a water reservoir. The collection surface was sloped toward the drain to facilitate the collection and removal of the droplets which precipitated. The water reservoir acted as a source of water vapor and also separated the collection surface from the side walls, further reducing the possibility of the walls influencing the processes occurring.

A one-half inch thick aluminum plate was used as the top of the chamber. The inner surface was covered by an absorbent cloth held in place by an aluminum frame. The cloth was kept moist during the tests to provide a source of water vapor. Four one-quarter inch diameter tubes in the top plate served as injection ports which were directed outward from the center of the chamber at 45° angles to produce rapid mixing in the chamber. The air was exhausted from the chamber through the central drain and through slots around the perifery.

During the tests, the top plate was maintained at room temperature and the bottom surface was cooled to the desired temperature by circulating water through the water jacket under the chamber. With a temperature difference of less than six degrees, no heat was required to keep the top plate temperature constant, but when higher temperature differences were used, warm water was circulated through a coil on top of the chamber to provide the heat required. The temperature of each surface was monitored by two tel-thermometer probes (Van Waters and

Rogers, Inc., #61254) accurate to 0.2°F, connected to a calibrated milliammeter.

2. The Aerosols

The aerosols used in this study were produced in the laboratory by atomizing known aqueous solutions of lead compounds with calibrated nebulizers and drying the resulting droplets. A deVilbus nebulizer was used to produce a relatively uniform spray of droplets three to four microns in diameter and a Coleman #21-300 atomizer was used to produce larger droplets seven to ten microns in diameter. The droplets were mixed with dry filtered air in a pair of drying chambers arranged in series to produce good drying and dilution. A drying time of five minutes was adequate to produce good drying, but was not long enough to allow a significant amount of coagulation to occur.

A multistage Andersen Sampler was used to determine the size distribution of the lead aerosols produced in the laboratory by the aerosol generators. The sampler, developed by the Andersen Consulting Service,[1] consisted of an aluminum cylinder containing a series of six stages through which the aerosol sample, mixed with room air, was consecutively drawn. The device was pressure sealed with gaskets and three adjustable spring fasteners. Each stage contained a glass impaction plate immediately below a perforated plate with 400 holes. The size of the holes was constant for each stage, but smaller in each successive stage. Air was drawn through the entire sampler at the rate of one cubic foot per minute and, due to the decreasing hole sizes, the velocity of the jets of air impinging on the impactor plates increased in each stage. When the velocity imparted to a particle carried by an air stream was sufficiently great, inertial forces overcame the aerodynamic drag and the particle did not follow the air stream which was deflected by the glass plate. Rather, the particle left the air stream and was impacted on the plate. The smaller particles remained in the air stream and were carried to the next stage. A clean-up filter consisting of a 47 millimeter #42 Whatman filter pad mounted in a Gelman #1302 in-line filter holder acted as the seventh stage to collect any particles too small to be impacted on the glass plates.

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[1] The Andersen Consulting Service, 1074 Ash Avenue, Provo, Utah.

The collection efficiency for each stage is defined as the ratio of the number of particles of a given size collected by the stage to the number of these particles incident on the stage. Flesch et al. (1966) used methylene blue and polystyrene aerosols and an electron microscope as a primary reference to determine the collection efficiencies for each stage of the sampler. Their results are shown in Figure 4-2, which shows the collection efficiencies as a function of the aerodynamic particle diameters. These curves indicate that there is considerable

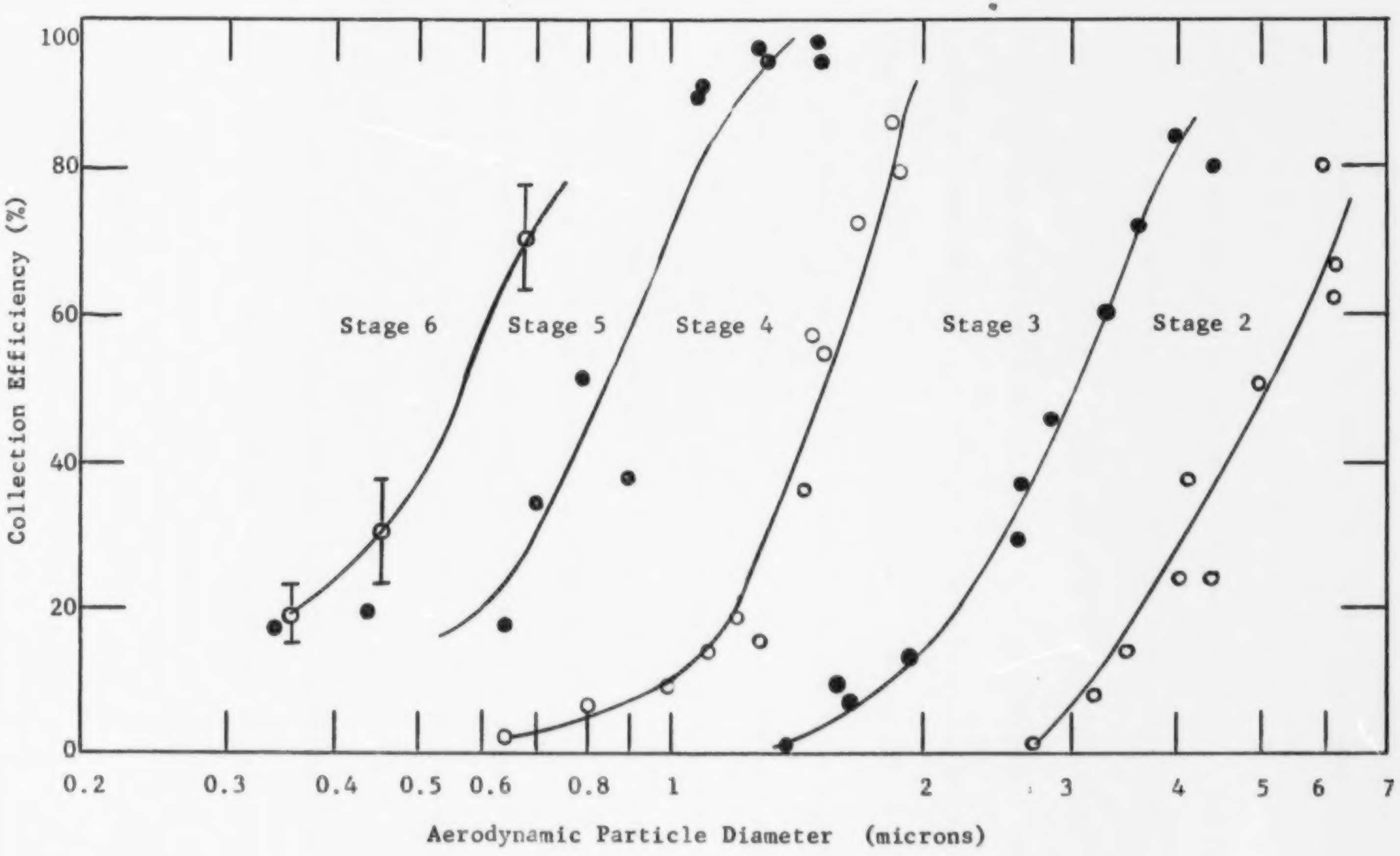

FIGURE 4-2
ANDERSEN SAMPLER COLLECTION EFFICIENCY CURVES (LEAST SQUARES FIT)
AND DATA POINTS FOR STAGES 2 - 6 (Flesch et al., 1966)

overlap between the stages. Some particles of a given size will be collected on several stages. To simplify this problem, the cut-off diameter for each stage was arbitrarily chosen as the diameter at which the collection efficiency was 50%. The choice of another cut-off efficiency would alter the distributions slightly.

All calibration curves for the Andersen Sampler are formulated in terms of the aerodynamic equivalent diameter of smooth unit density spheres. The relationship used to convert these aerodynamic diameters to the actual diameters of the lead compound aerosols used in the laboratory is:

$$d_{Aero} = d_{Act}(\rho c)^{1/2} \quad \text{(Flesch et al., 1966)} \qquad (4\text{-}1)$$

where

d_{Aero} = the diameter of an aerodynamically equivalent smooth spherical particle of unit density, (cm)

ρ = density of the particle, (g/cm^3)

c = the dimensionless Cunningham slip correction $1.00 + 0.16 \times 10^{-4}/d_{Act}$

d_{Act} = actual particle diameter, assuming smooth spherical particles, (cm)

This equation and the curves in Figure 4-2 were used to calculate the cut-off diameters for each stage when various lead aerosol particles were passed through the sampler. The results of these calculations are given in Table 4-2.

TABLE 4-2

CALIBRATION OF LEAD COMPOUND AEROSOL SIZES

Stage	Aerodynamic Cut-off Diameter (μ)	Actual Cut-off Diameter (μ)			
		$PbBr_2$	PbI_2	$PbCl_2$	$Pb(NO_3)_2$
1	8.0	3.00	3.20	3.25	3.50
2	5.35	2.00	2.10	2.14	2.42
3	2.95	1.07	1.13	1.14	1.30
4	1.75	0.60	0.64	0.66	0.75
5	0.92	0.28	0.30	0.31	0.36
6	0.54	0.13	0.15	0.16	0.19

The size of the aerosol particles produced in the laboratory was dependent on the nebulizer used, the lead compound density, and the concentration of the compound in the solution atomized. The volume, V, of a droplet produced by the nebulizer was

$$V = 4/3\ \pi R^3$$

where R is the radius of the droplet. The amount of the lead compound, V_L, in this droplet was then

$$V_L = \frac{c}{1000} \cdot \frac{1}{\rho} V$$

where c is the number of grams of compound in a liter of the solution atomized, and ρ is the density of the compound.

The radius, r, of the particle formed by drying the droplet was then

$$\begin{aligned} r &= (V_L/4/3\ \pi)^{1/3} \\ &= \left[\frac{\frac{c}{1000\rho}\,(4/3\ \pi R^3)}{4/3\ \pi}\right]^{1/3} \\ &= 0.1 \left(\frac{c}{\rho}\right)^{1/3} R \qquad (4\text{-}2) \end{aligned}$$

The solution concentrations were adjusted so that each solution produced dry aerosols with similar size distributions. However, due to the relatively insoluble nature of lead iodide, less concentrated solutions of this compound had to be used, resulting in slightly smaller aerosol particles.

The aerosols were tested for dryness with the Andersen Sampler and the results are summarized in Tables 4-3 and 4-4. The actual diameters, D_{Act}, recorded are the mass median diameters exhibited by the various aerosols, and the theoretical diameters, D_{Theo}, are the diameters which were calculated from equation (4-2). The size distributions were checked for uniformity by plotting the sampler data on log-probability paper. The size distribution data are contained in Tables 4-5 and 4-6, and the log-probability plots are shown in Figures 4-3 and 4-4. The linear relationships suggested that the size distributions were log-normal. A deficiency in the number of large droplets was indicated by the deviation from the linear curve at large diameters. This skewed effect is to be expected with spray-generated aerosols (Mugele et al., 1951). The size distributions for the wet aerosols were also determined by spraying the droplets directly into the air stream to be sampled. It was assumed that no significant drying occurred during the sampling. The wet aerosols also exhibited a log-normal distribution similar to the dry aerosol distribution. This indicated that uniform drying was being achieved without a significant amount of coagulation occurring.

TABLE 4-3

AEROSOL MASS MEDIAN DIAMETERS (DILUTE SOLUTIONS)

Compound	c (g/l)	ρ (g/cc)	deVilbus Nebulizer D_{Theo} (μ)	deVilbus Nebulizer D_{Act} (μ)	Coleman Nebulizer D_{Act} (μ)
$PbBr_2$	1.87	6.66	0.230	0.29	0.50
$PbCl_2$	1.64	5.85	0.230	0.24	0.50
PbI_2	0.82	6.16	0.180	0.21	---
$Pb(NO_3)_2$	1.27	4.53	0.230	0.26	0.50

TABLE 4-4

AEROSOL MASS MEDIAN DIAMETERS (CONCENTRATED SOLUTIONS)

Compound	c (g/l)	ρ (g/cc)	deVilbus Nebulizer D_{Theo} (μ)	Coleman Nebulizer D_{Theo}* (μ)
$PbBr_2$	8.1	6.66	0.37	0.86
$PbCl_2$	9.3	5.85	0.41	0.93
$Pb(NO_3)_2$	8.8	4.53	0.48	1.00

* D_{Theo} was calculated assuming 8.0 μ as the mass median diameter of droplets produced by the Coleman Nebulizer.

TABLE 4-5

AEROSOL SIZE DISTRIBUTION
DeVilbus Nebulizer

	Stage	Cut-off Diameter	μgPb	Percent of Sample	Cummulative Percent
$PbBr_2$	1	3.00			
	2	2.00	0.7	5.6	5.6
	3	1.07			
	4	0.60	3.0	24.0	29.6
	5	0.28			
	6	0.13	4.8	38.5	68.1
	7	----	4.0	31.9	100.0
			12.5		
$PbBr_2$	1	3.00			
	2	2.00	1.3	11.5	11.5
	3	1.07			
	4	0.60	2.3	20.3	31.8
	5	0.28			
	6	0.13	4.4	39.0	70.8
	7	----	3.3	29.2	100.2
			11.3		
PbI_2	1	3.20			
	2	2.10	0		
	3	1.13			
	4	0.64	1.5	20.8	20.8
	5	0.30			
	6	0.15	2.9	40.2	61.0
	7	----	2.8	39.0	100.0
			7.2		
PbI_2 (No Drying)	1	8.0	1.2	9.6	9.6
	2	5.35	3.1	24.8	34.4
	3	2.95	2.7	21.6	56.0
	4	1.75	1.9	14.9	70.9
	5	0.92	1.4	11.1	82.0
	6	0.54	1.0	8.4	90.4
	7	----	1.2	9.6	100.0
			12.5		

TABLE 4-5, Continued

	Stage	Cut-off Diameter	ugPb	Percent of Sample	Cummulative Percent
$PbCl_2$	1	3.25			
	2	2.14	0.5	4.6	4.6
	3	1.14			
	4	0.66	2.2	20.3	24.9
	5	0.31			
	6	0.16	4.2	38.6	63.5
	7	----	4.0	36.5	100.0
			10.9		
$PbCl_2$	1	3.25			
	2	2.14	0.5	4.0	4.0
	3	1.14			
	4	0.66	2.1	16.8	20.8
	5	0.31			
	6	0.16	4.7	37.5	58.3
	7	----	5.2	41.7	100.0
			12.5		
$Pb(NO_3)_2$	1	3.50			
	2	2.42	1.0	8.5	8.5
	3	1.30			
	4	0.75	1.6	13.5	22.0
	5	0.36			
	6	0.19	5.0	42.1	64.1
	7	----	4.2	35.9	100.0
			11.8		
$Pb(NO_3)_2$	1	3.50			
	2	2.42	0.5	4.8	4.8
	3	1.30			
	4	0.75	1.5	14.4	19.3
	5	0.36			
	6	0.19	3.6	34.6	53.9
	7	----	4.8	46.1	100.0
			10.4		

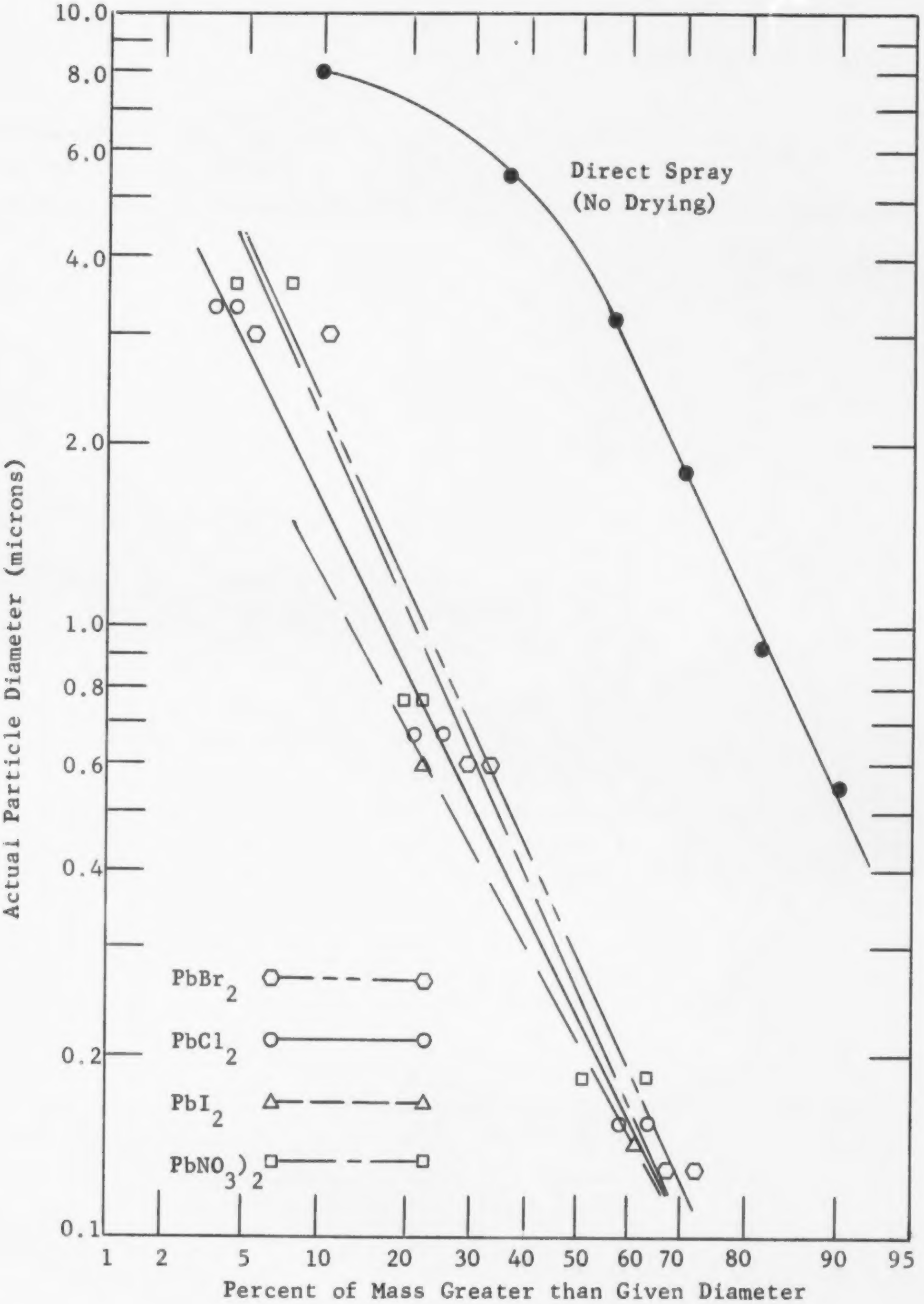

FIGURE 4-3
AEROSOL SIZE DISTRIBUTION (DE VILBUS NEBULIZER)

TABLE 4-6

AEROSOL SIZE DISTRIBUTION
Coleman Nebulizer

	Stage	Cut-off Diameter	μgPb	Percent of Sample	Cummulative Percent
PbCl$_2$	1	3.25	1.5	1.6	1.6
	2	2.21	2.3	2.5	4.1
	3	1.17	14.5	15.4	19.5
	4	0.67	16.5	17.6	37.1
	5	0.32	18.3	19.5	56.6
	6	0.16	18.7	19.9	76.5
	7	----	22.2	23.5	100.0
			94.0		
PbCl$_2$	1	3.25	2.1	1.6	1.6
	2	2.21	3.9	2.9	4.5
	3	1.17	18.6	13.9	18.4
	4	0.67	31.5	23.5	41.9
	5	0.32	34.6	25.8	67.7
	6	0.16	11.8	9.0	76.7
	7	----	31.3	23.3	100.0
			133.8		
PbCl$_2$	1	3.25	2.0	1.8	1.8
	2	2.21	2.5	2.2	4.0
	3	1.17	10.6	9.5	13.5
	4	0.67	23.5	20.9	34.4
	5	0.32	35.5	31.7	66.1
	6	0.16	13.9	12.4	78.5
	7	----	24.2	21.5	100.0
			112.2		

TABLE 4-6, Continued

	Stage	Cut-off Diameter	μgPb	Percent of Sample	Cummulative Percent
$Pb(NO_3)_2$	1	3.50	2.6	2.0	2.0
	2	2.42	6.4	4.9	6.9
	3	1.30	13.2	10.1	17.0
	4	0.75	19.3	14.9	31.9
	5	0.36	30.6	23.3	55.2
	6	0.19	22.8	17.5	72.7
	7	----	35.4	27.3	100.0
			130.3		
$Pb(NO_3)_2$	1	3.50	5.2	4.7	4.7
	2	2.42	3.7	3.3	8.0
	3	1.30	6.8	6.1	14.1
	4	0.75	21.1	19.1	33.2
	5	0.36	26.5	24.0	57.0
	6	0.19	22.0	19.8	76.8
	7	----	26.0	23.5	100.0
			111.3		

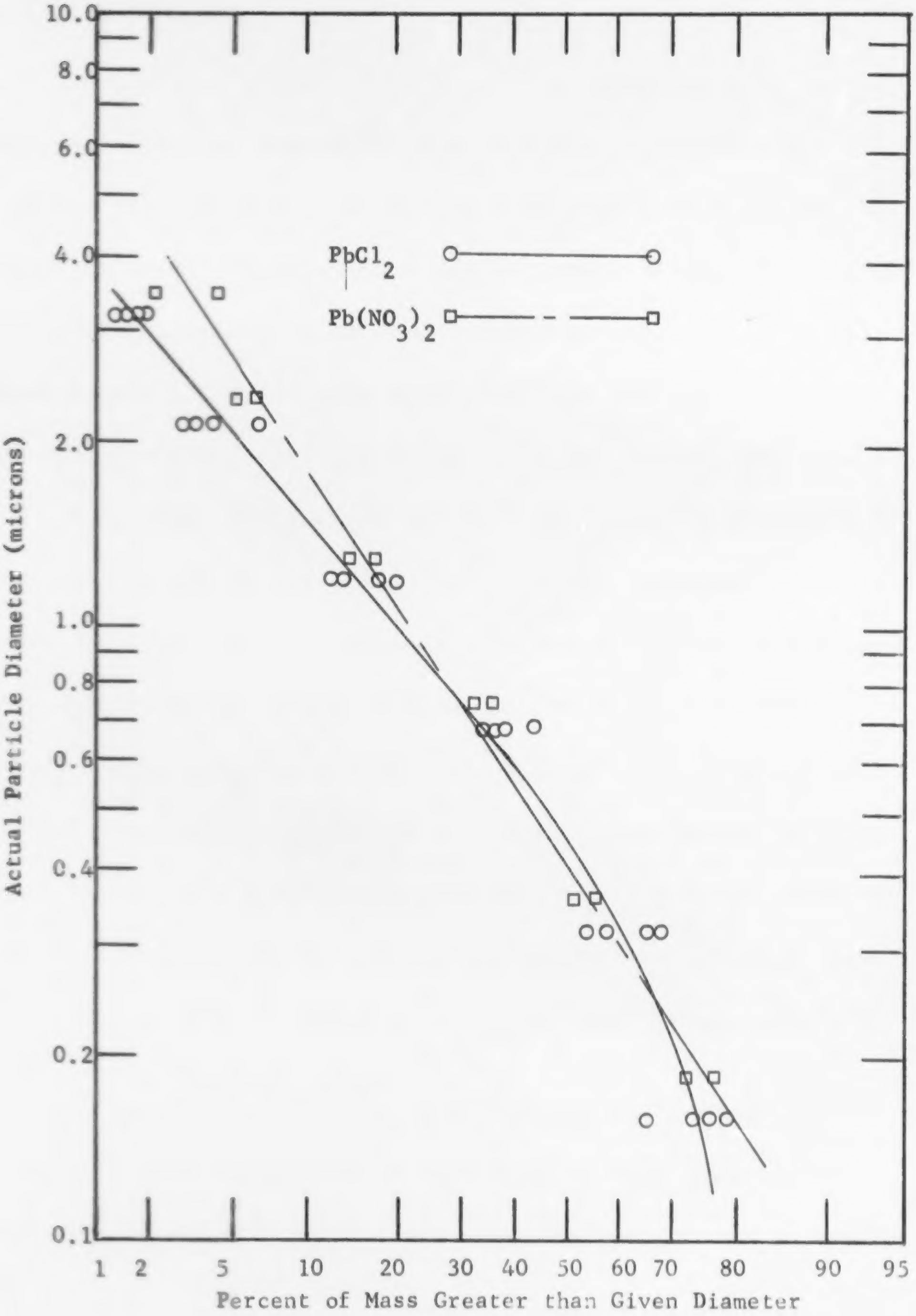

FIGURE 4-4
AEROSOL SIZE DISTRIBUTION (COLEMAN NEBULIZER)

3. The Equipment

Figure 4-5 is a schematic diagram showing the aerosol generating equipment and the supersaturation chamber. Also shown is a light beam used to illuminate a small volume in the chamber. The light beam was produced by focusing the light from a PEK Laboratories[1] #202 mercury arc lamp through two achromatic condensing lenses. A stable power supply (PEK Laboratories #704) was used to maintain a constant intensity. The beam illuminated a well defined volume in the chamber, 0.3 centimeters in diameter. The droplets in this volume were photographed using a short focus lens (135 millimeter) on a Speed Graphic camera (not shown) mounted at 90° to the light path. Extremely high speed film (Kodak Royal X Pan, ASA 1250) and extended development allowed pictures of the small droplets to be taken with exposures of 1/25 of a second. The photographs were used to determine the size and number density of the droplets in the chamber. The droplets recorded on the film were counted and measured using a Gaertner measuring microscope.[2]

4. Nucleation Test Procedure

To produce uniform conditions in the chamber during the aerosol tests, a reproducible procedure was established. The chamber was

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[1] Sunnyvale, California

[2] Manufactured by the Gaertner Scientific Corporation, Chicago, Illinois.

AEROSOL GENERATOR AND SUPERSATURATION CHAMBER

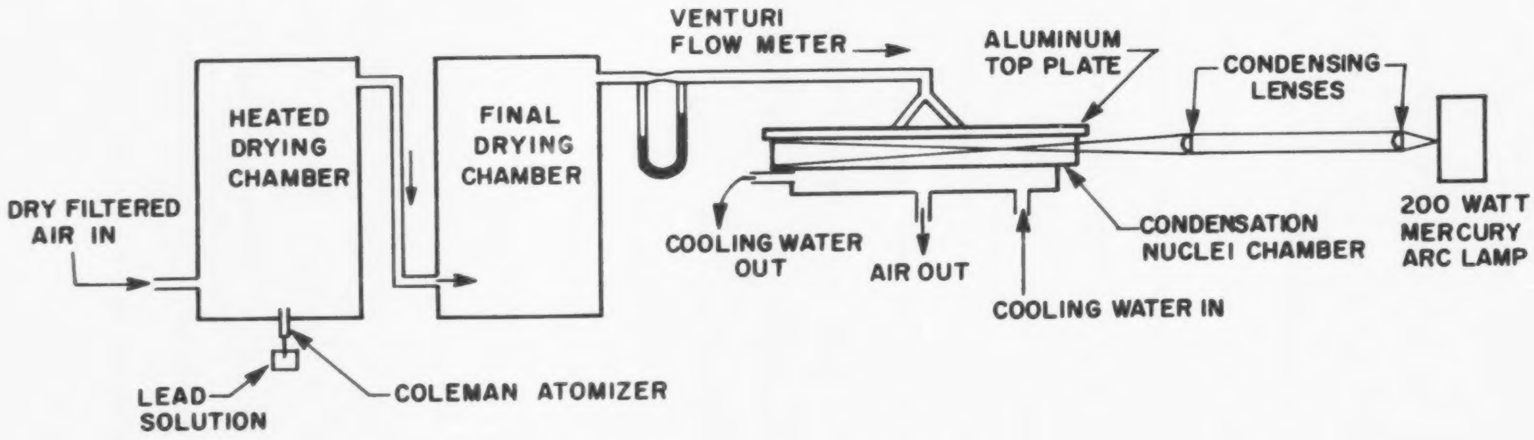

DRY FILTERED AIR IN
HEATED DRYING CHAMBER
LEAD SOLUTION
COLEMAN ATOMIZER
FINAL DRYING CHAMBER
VENTURI FLOW METER
COOLING WATER OUT
AIR OUT
ALUMINUM TOP PLATE
COOLING WATER IN
CONDENSATION NUCLEI CHAMBER
CONDENSING LENSES
200 WATT MERCURY ARC LAMP

FIGURE 4-5

prepared by rinsing all surfaces with distilled water, including the moist cloth covering the inner surface of the top plate. The collection surface was scrubbed with a rubber policeman and 6 N nitric acid and rinsed again with distilled water. The water reservoir was filled with water to a depth of one millimeter. The central drain was closed and the collection surface was covered with distilled water. The top plate was put into place and cooling was started through the water bath. When the desired temperature difference was reached, and equilibrium conditions were established, the drain was opened. The water covering the collection surface drained out, carrying with it any contaminates that were trapped in the chamber when the top plate was put into place. Dry filtered air was injected into the chamber through the top ports to replace the water. This air flow was continued for several minutes to establish equilibrium in the chamber.

The dry aerosol from the drying chambers was injected into the air stream and the flow rate was maintained at three liters per minute. The injection continued for five minutes. The aerosol was then stopped and clean air continued to flow for five more minutes. After this time, all particles in the chamber had been exhausted or removed by sedimentation. The air flow was stopped and the top plate was removed.

The drain was immediately rinsed twice with distilled water to remove any lead that had collected there. Finally, the bottom surface was cleaned with alternate washings of 6 N nitric acid and distilled water and scrubbed with a rubber policeman. These washings were collected in 125 milliliter Erlynmeyer flasks and analyzed for lead content.

The droplet cloud which was formed in the chamber was photographed after five minutes of aerosol injection, just before the aerosol injection was stopped. Photographs taken after two, three, four and five minutes of injection showed that the droplet size and number density remained relatively constant during the period of aerosol injection.

Lead Analysis

The procedure used in this study to determine the lead content of the samples was a colorimetric test employing the use of chloroform for extracting the lead from a basic citrate-cyanide buffer solution. Diphenylthiocarbazone was used as an indicator. The basic procedure was developed by Mr. Louis J. Snyder of the Ethyl Corporation.

1. Equipment

The samples were prepared in 125 milliliter Erlynmeyer flasks and the extraction was performed in 125 milliliter separatory funnels. The color intensity was determined using a Beckman Model DB spectrophotometer.

2. Reagents

The following reagents used in this procedure were prepared using reagent grade stock chemicals:

1. Citrate-Cyanide Solution--A buffer solution prepared by dissolving 400 grams of dibasic ammonium citrate in 500 milliliters of distilled water, followed by 30 grams of sodium cyanide and 20 grams of sodium sulfite. The mixture was then diluted to one liter.
2. Indicator Solution--Sixty milligrams of diphenylthiocarbazone (dithizone) dissolved in one liter of C. P. chloroform (stored in a refrigerator).
3. Nitric Acid Solution--Two hundred milliliters of concentrated nitric acid diluted to one liter with distilled water.
4. Mixed Acid Solution--Six hundred milliliters of concentrated acid mixed with 400 milliliters of 72% perchloric acid.
5. Stock Lead Solution--1.5984 grams of lead nitrate (dried at 105°C) dissolved in one liter of 1% nitric acid. This solution contained one milligram of lead per milliliter of solution.
6. Standard Lead Solution--One milliliter of stock lead solution diluted to one liter with 1% nitric acid. This solution contained one microgram of lead per milliliter of solution.

3. Analytical Procedure

All samples were transferred to 125 milliliter Erlynmeyer flasks (filter paper samples were first dissolved in 6 N nitric acid). Five milliliters of the Mixed Acid Solution were added and the samples were placed on a hot plate in a hood and slowly evaporated until the dense white fumes of perchloric acid appeared, indicating that all organic materials in the samples were destroyed. The samples were cooled and 10 milliliters of the Nitric Acid Solution were added. This was then transferred to 125 milliliter separatory funnels and the flasks were rinsed with distilled water which was also transferred to the funnels. One hundred milliliters of the Citrate-Cyanide Solution were mixed with 200 milliliters of concentrated ammonium hydroxide, and 25 milliliters of this solution were added to each flask and transferred to the funnels. The contents of the funnels were mixed and allowed to cool.

Five milliliters of the Indicator Solution were then added and the solution thoroughly mixed by shaking the funnels for one minute. The phases were allowed to separate and the absorbance of the chloroform layer was determined on the spectrophotometer at a wave length of 510 millimicrons. If the absorbence was too high (above 1.500), 25 milliliters of the buffer-ammonium hydroxide solution and five milliliters of the Indicator Solution were added. After shaking, the absorbance was again determined.

4. Calculations

Blank samples were run with each set of samples and standards were run periodically. The standards were taken from 1% nitric acid solutions containing a known concentration of lead. They were subjected to the same procedures as the actual samples. The results obtained from the standards were plotted to produce a linear standard curve. One curve was developed for the tests where five milliliters of indicator were used and another was developed for the 10 milliliter case. The net absorbance of each sample (or standard) was determined by subtracting the absorbance of the blank from the absorbance determined on the spectrophotometer. This absorbance was entered on the standard curve and the amount of lead present was determined.

A good indication of the precision which resulted from this procedure is given by the reproducability of the blank and standard curves. The data in Tables 4-7 and 4-8 summarizes calibration measurements taken during this study on standards containing five, 10 and 15 micrograms of lead. The slope of the standard curve for five milliliters of indicator was 6.6 absorbance units per microgram of lead. The corresponding slope for 10 milliliters of indicator was 3.3 absorbance units per microgram of lead.

The values obtained for the blanks and standards are very dependent on the purity of the chemicals used in the analysis and the care

TABLE 4-7

LEAD ANALYSIS STANDARD CURVE (5 MILLILITER OF INDICATOR)

Date	Blank_1	Blank_2	$5\ \mu g_1$	$5\ \mu g_2$	$10\ \mu g$	$15\ \mu g$
6-28-66	0.43	0.45	0.76	0.76	1.05	1.35
6-29-66	0.40	0.43	0.76	0.73	1.10	1.42
7-2-66	0.38	0.38	0.73	0.76	1.05	1.40
7-3-66	0.39	0.43	0.75	0.73	1.04	1.44
7-4-66	0.41	0.39	0.72	0.83	1.06	1.36
8-8-66	0.44	0.40	0.74	0.72	1.04	1.35
8-8-66	0.41	0.36	0.71	0.76	1.09	1.34
9-21-66	0.40	0.38	0.74	0.73	1.06	1.38
9-21-66	0.39	0.38	0.70	0.74	1.06	1.40
12-6-66	0.40	0.41	0.72	0.75	1.05	1.41
1-16-67	0.43	0.40	0.77	0.72	1.08	1.43
3-22-67	0.37	0.38	0.70	0.74	1.06	1.39
4-7-67	0.38	0.40	0.74	0.77	1.06	1.40
6-13-67	0.43	0.39	0.76	0.74	1.08	1.44
7-26-67	0.41	0.40	0.73	0.73	1.07	1.41
8-10-67	0.43	0.40	0.74	0.73	1.06	1.43
11-16-67	0.39	0.36	0.72	0.77	1.03	1.39
12-11-67	0.37	0.40	0.73	0.75	1.03	0.38
1-15-68	0.41	0.43	0.75	0.71	1.11	1.33
2-21-68	0.40	0.37	0.71	0.74	1.04	1.34
		16.05		29.57	21.20	27.75
AVERAGE		0.40		0.74	1.06	1.38
STANDARD DEVIATION		0.022		0.023	0.024	0.035

TABLE 4-8

LEAD ANALYSIS STANDARD CURVES (10 MILLILITERS OF INDICATOR)

Date	Blank$_1$	Blank$_2$	5 μg$_1$	5 μg$_2$	10 μg	15 μg
7-28-66	0.35	0.33	0.50	0.53	0.68	0.88
7-29-66	0.33	0.38	0.49	0.49	0.71	0.89
8-2-66	0.29	0.35	0.53	0.57	0.65	0.87
8-3-66	0.38	0.36	0.50	0.54	0.68	0.89
8-4-66	0.36	0.38	0.53	0.56	0.72	0.86
9-8-66	0.34	0.38	0.50	0.54	0.70	0.86
10-21-66	0.35	0.39	0.50	0.49	0.71	0.87
6-3-67	0.29	0.33	0.50	0.53	0.69	0.91
11-16-67	0.31	0.35	0.51	0.51	0.68	0.88
		6.25		9.32	6.22	7.91
AVERAGE		0.35		0.52	0.69	0.88
STANDARD DEVIATION		0.04		0.03	0.02	0.02

taken in preparing the reagents. To ensure consistent readings, the same brands of chemicals were used to prepare new reagents, and blanks and standards were periodically run to detect any variations.

CHAPTER FIVE

EXPERIMENTAL RESULTS

Field Studies

Air, dry fallout and rainfall samples were collected in Palo Alto to determine the extent of lead pollution in the area, and to provide a basis for estimating the effectiveness of several natural atmospheric cleansing processes on the lead contaminants present. Since changes in meteorological conditions may have significant effects on the atmospheric cleansing processes and the amounts of pollutants present at a given site, a large number of samples were taken over an extended period of time. Over 400 samples were collected during the 22 month period from August 1966 through May 1968. Average values have been determined whenever possible to minimize the effects of atmospheric variability. The data from each portion of the field program are presented separately.

1. Air Samples

Air samples were filtered periodically to determine the concentration of airborne lead pollutants at the sampling sites. The lead concentration in each sample was obtained from the chemical determination of the total amount of lead collected on the filter paper and the measured volume of air drawn through the pump. In most cases, the high volume filter pumps provided adequate levels of lead in sampling periods as short as five minutes; therefore, the concentrations have been reported as instantaneous values. The concentrations obtained from samples taken over longer periods of time have been reported as average levels. The high lead levels, and the sensitive analytical techniques used, allowed accurate determinations of lead concentrations to be made. Estimating the volume of air drawn through the filter was the major source of error in the air sampling procedure. The float gages on the pumps could only be read to the nearest cubic foot per minute, and the gages themselves were not extremely accurate. However, the air volumes reported are probably within five per cent of the true values.

The air sample data show that lead pollutants are present in the atmosphere at all three sites. These data are contained in Appendix A. The freeway samples contained lead concentrations which varied from 0.3 $\mu g/m^3$ in the early morning hours to 19 $\mu g/m^3$ during peak traffic periods. Variations from 1.5 $\mu g/m^3$ to 5.1 $\mu g/m^3$ were observed at the residential sites. Since the most pronounced variations and highest contaminant levels occurred at the freeway site, a large number of air samples were collected there, and fewer samples were taken at the other sites where the lead concentrations did not vary as rapidly or extensively.

Figures 5-1 through 5-4 are plots of the hourly lead concentrations observed at the freeway site in the late summer and fall of 1966. During this period of the year, atmospheric turbulence is usually lowest, and the decreased mixing results in higher concentrations of atmospheric pollutants. The traffic flow and wind velocity during each five minute sampling period are also shown on these plots. Figures 5-5 and 5-6 are plots of the hourly lead concentrations observed simultaneously at all three sites. The extent of the concentration variations can be seen easily. The lead levels at the freeway often changed by an order of magnitude in less than two hours, while the levels at the residential and foothill sites changed by only 200 to 300%.

The results of air samples taken at the freeway site in the Spring, when atmospheric mixing is usually greatest, are plotted in Figure 5-7. During periods when no rainfall was occurring, the maximum lead concentration observed was $9.3\ \mu g/m^3$, slightly less than 50% of the maximum level observed in the Fall. During periods of light to moderate rainfall, the maximum concentration observed was $7.4\ \mu g/m^3$. These air samples were taken only during the morning hours, because later in the day strong and gusty winds developed which caused rapid and erratic variations in lead concentrations.

Robinson et al. (1963) determined the atmospheric lead levels at several locations in the cities of San Francisco and Los Angeles and in

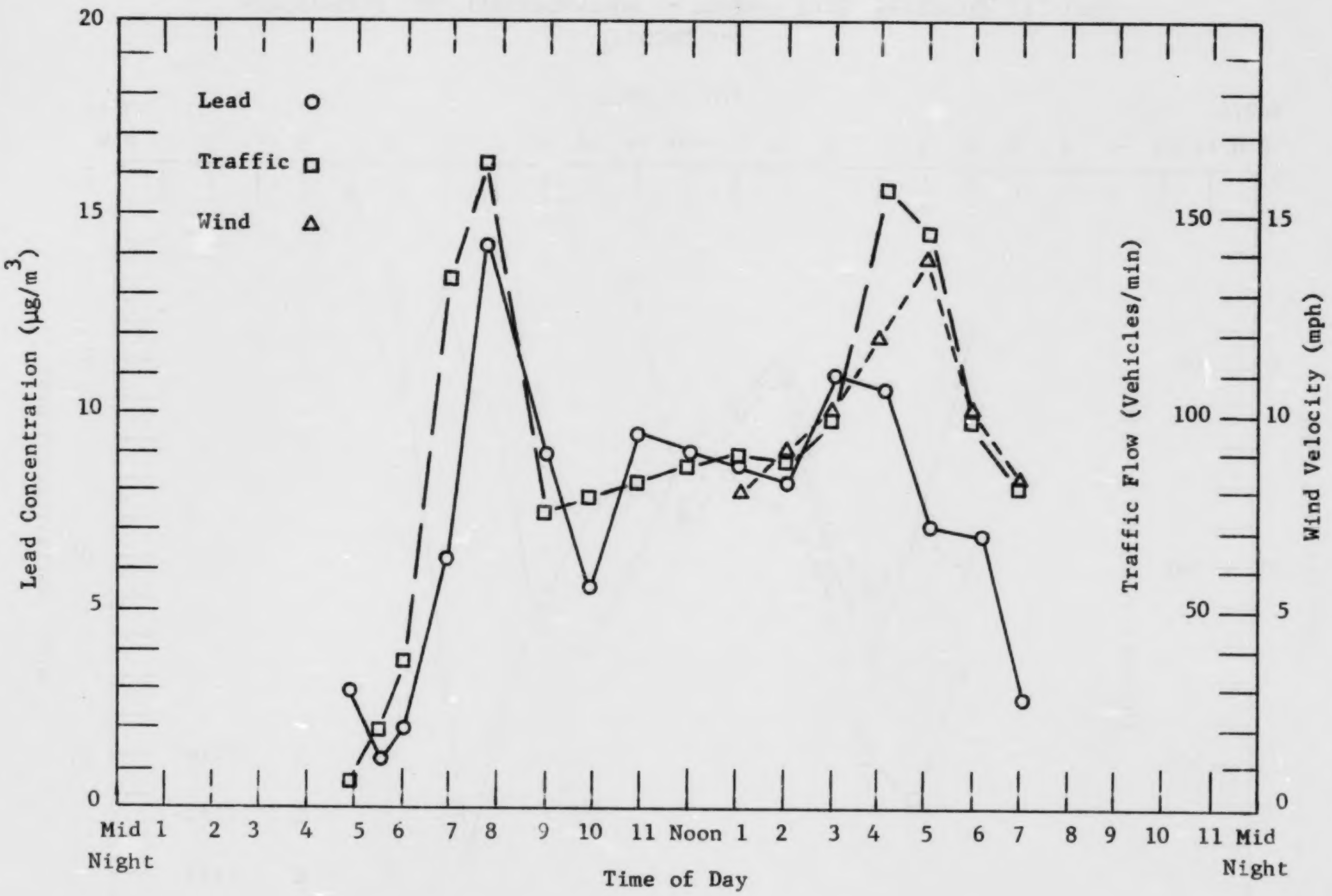


FIGURE 5-1
ATMOSPHERIC LEAD CONCENTRATION -- FREEWAY SITE, AUGUST 15, 1966

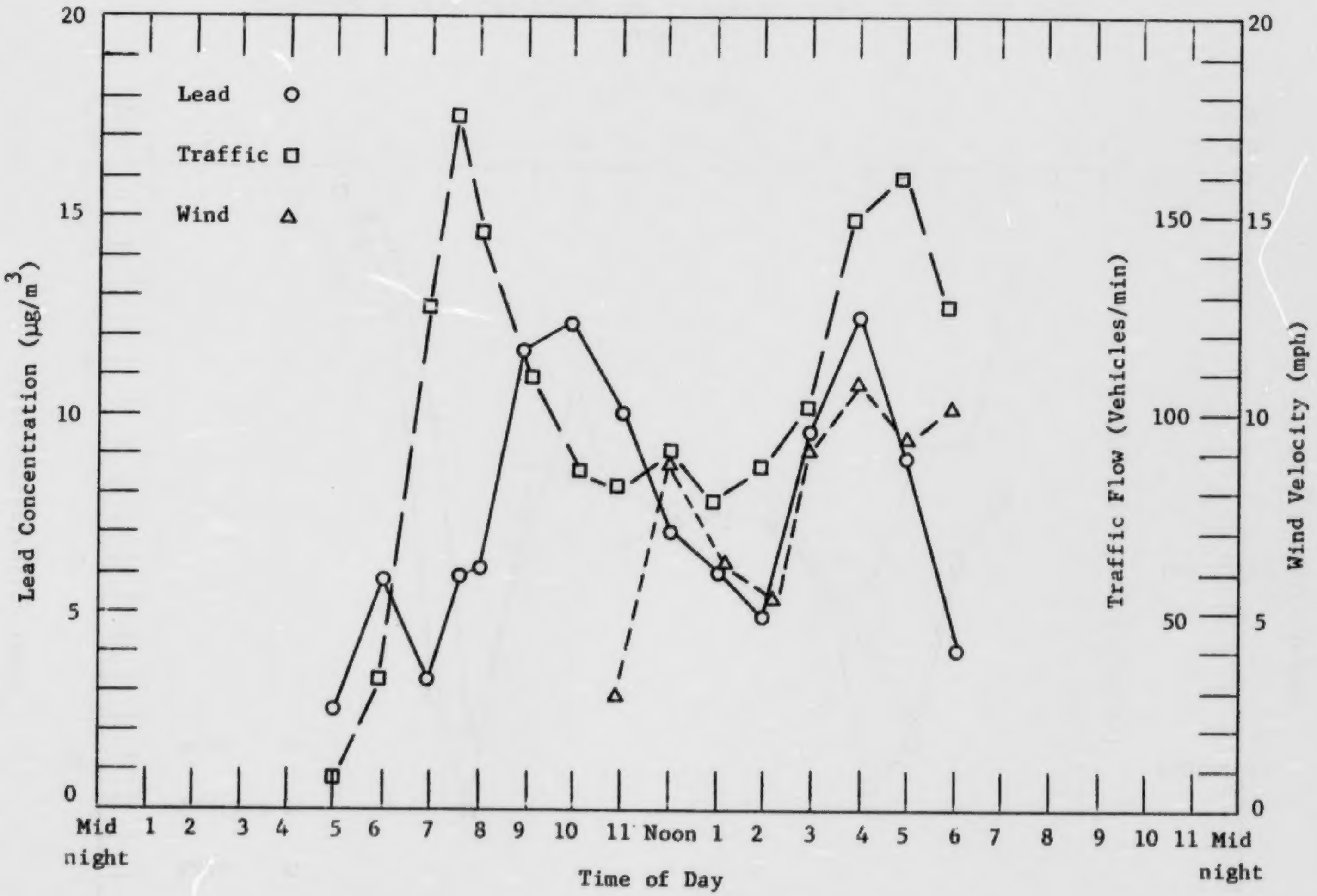


FIGURE 5-2
ATMOSPHERIC LEAD CONCENTRATION -- FREEWAY SITE, SEPTEMBER 12, 1966

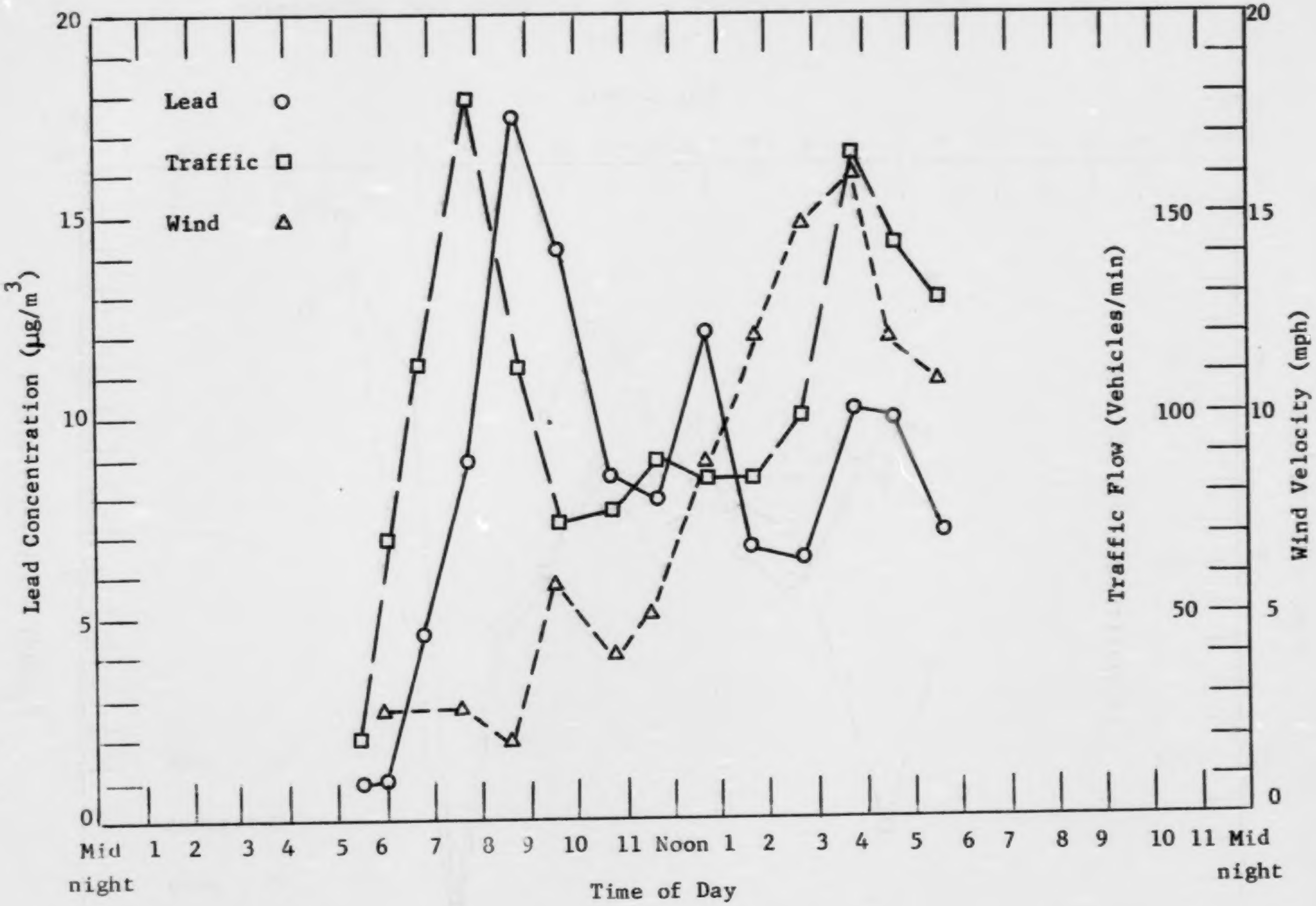


FIGURE 5-3
ATMOSPHERIC LEAD CONCENTRATION -- FREEWAY SITE, SEPTEMBER 30, 1966

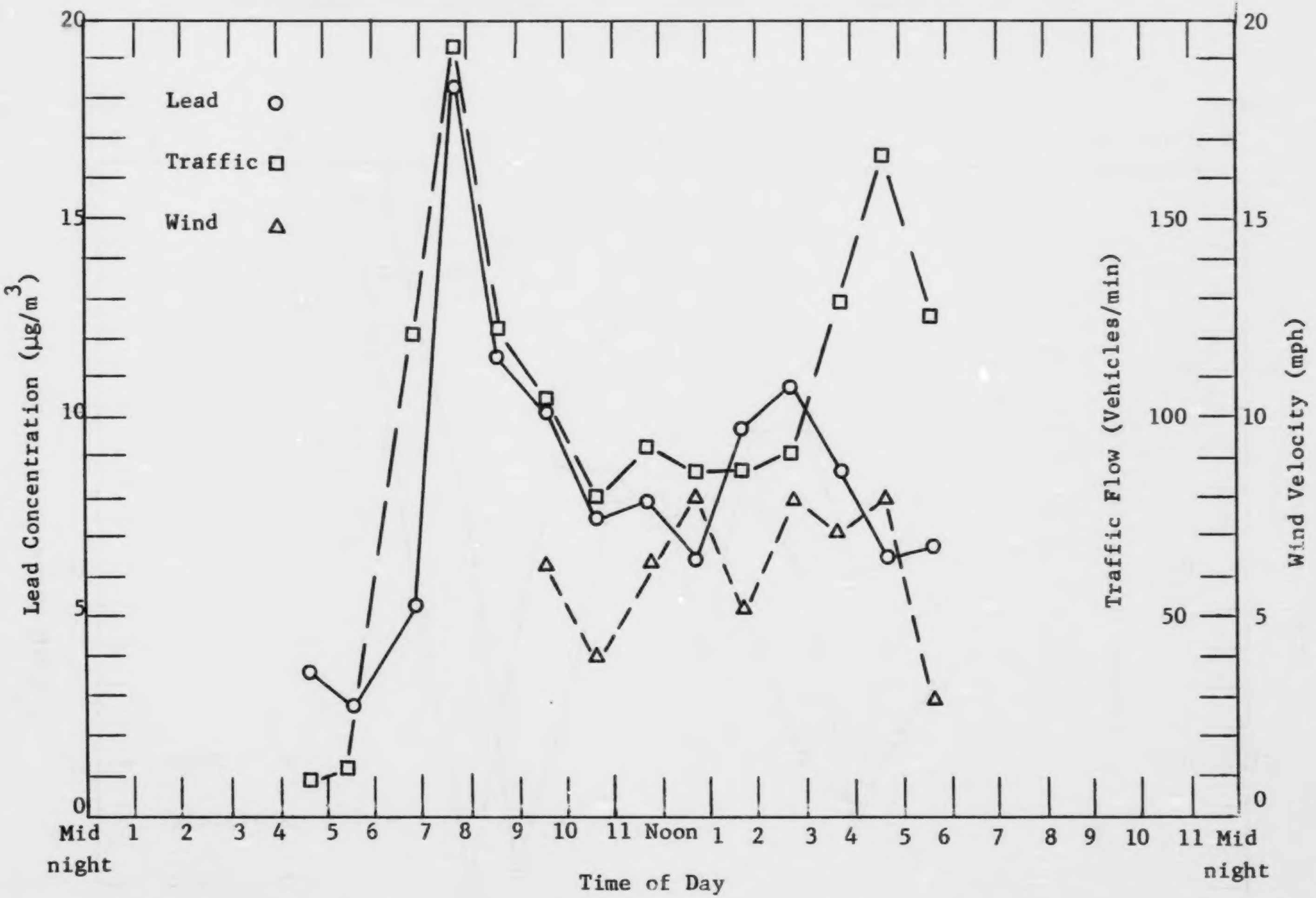


FIGURE 5-4
ATMOSPHERIC LEAD CONCENTRATION -- FREEWAY SITE, NOVEMBER 3, 1966

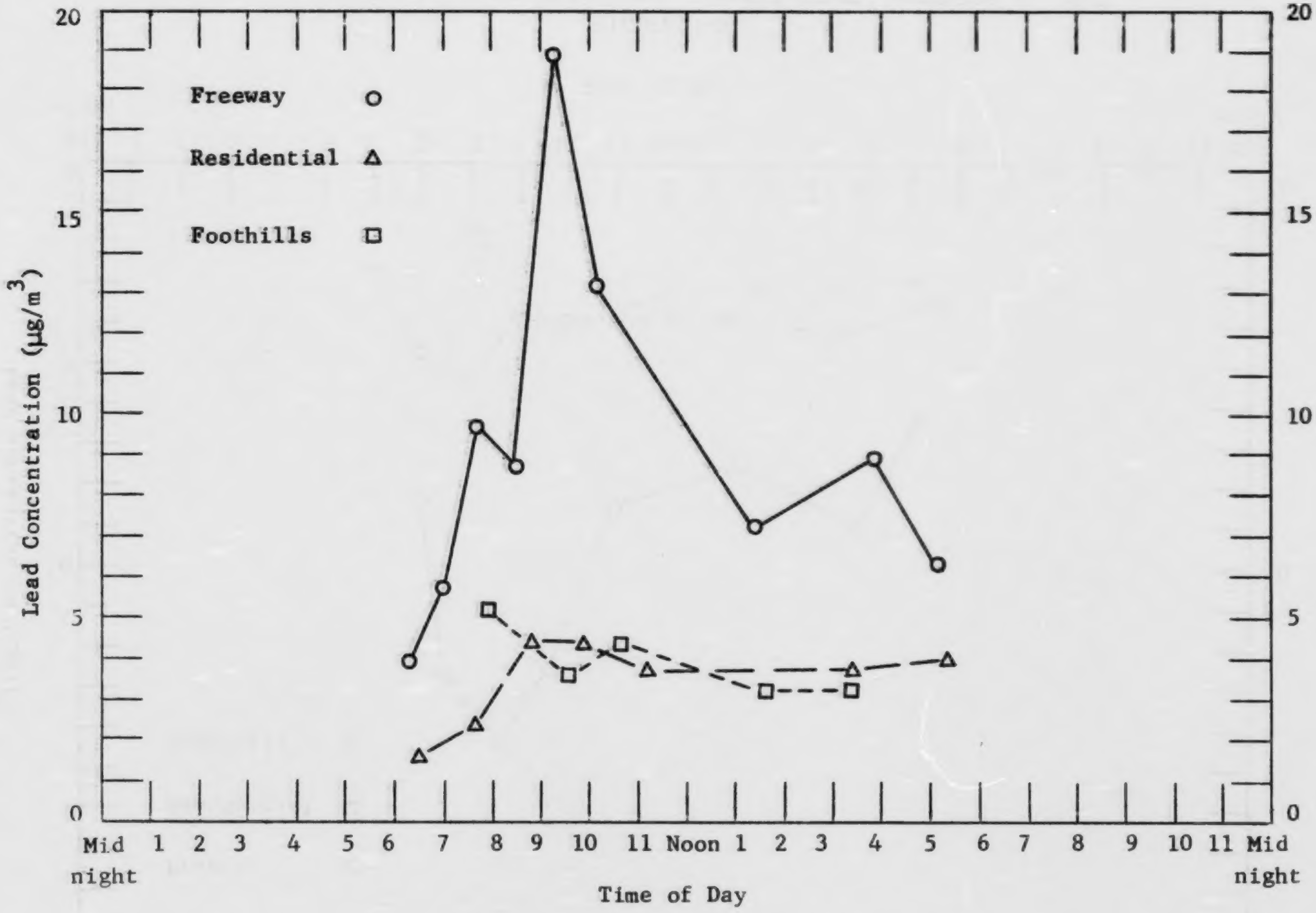


FIGURE 5-5
ATMOSPHERIC LEAD CONCENTRATION -- THREE SITES, SEPTEMBER 1, 1967

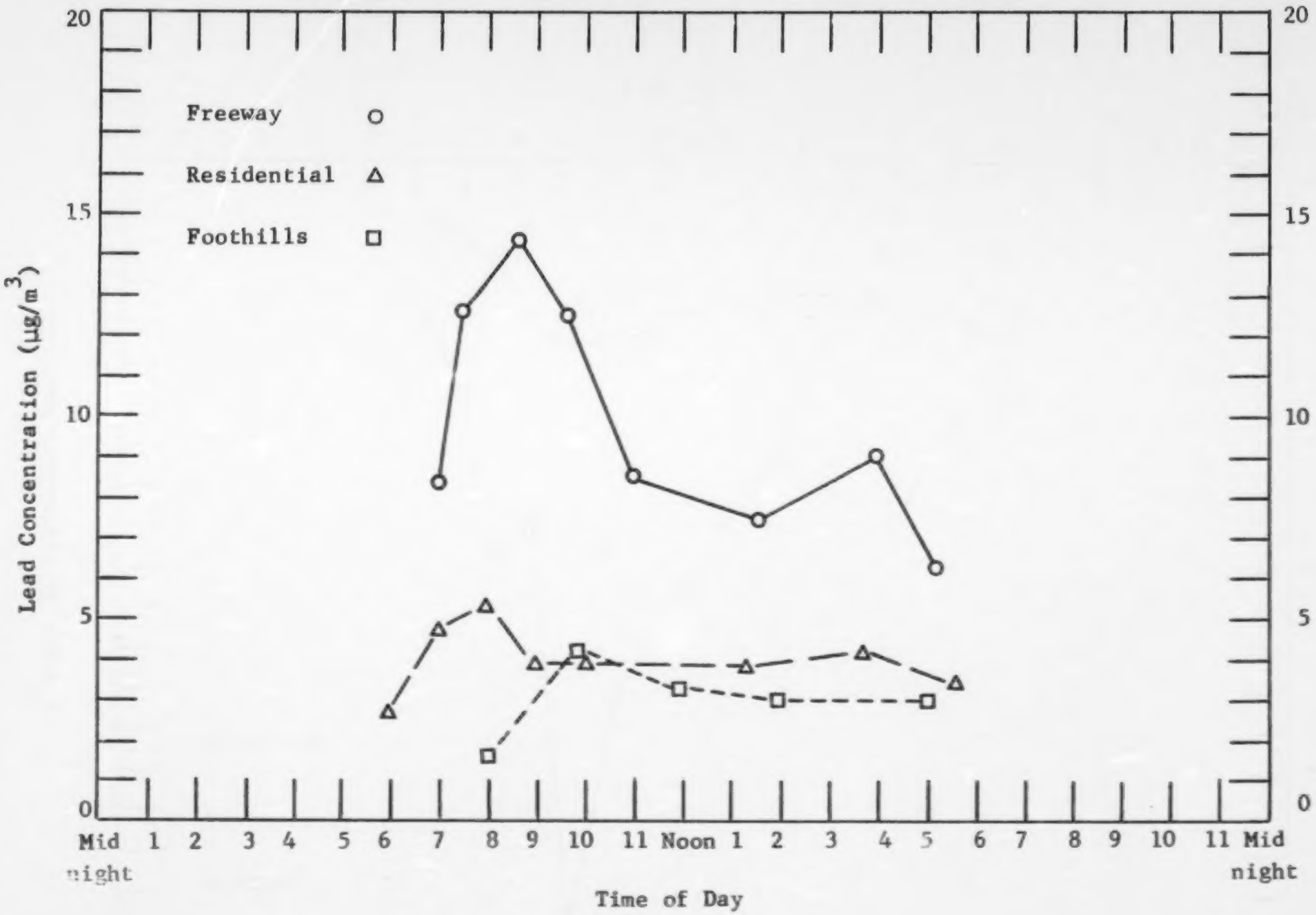


FIGURE 5-6
ATMOSPHERIC LEAD CONCENTRATION -- THREE SITES, NOVEMBER 7, 1967

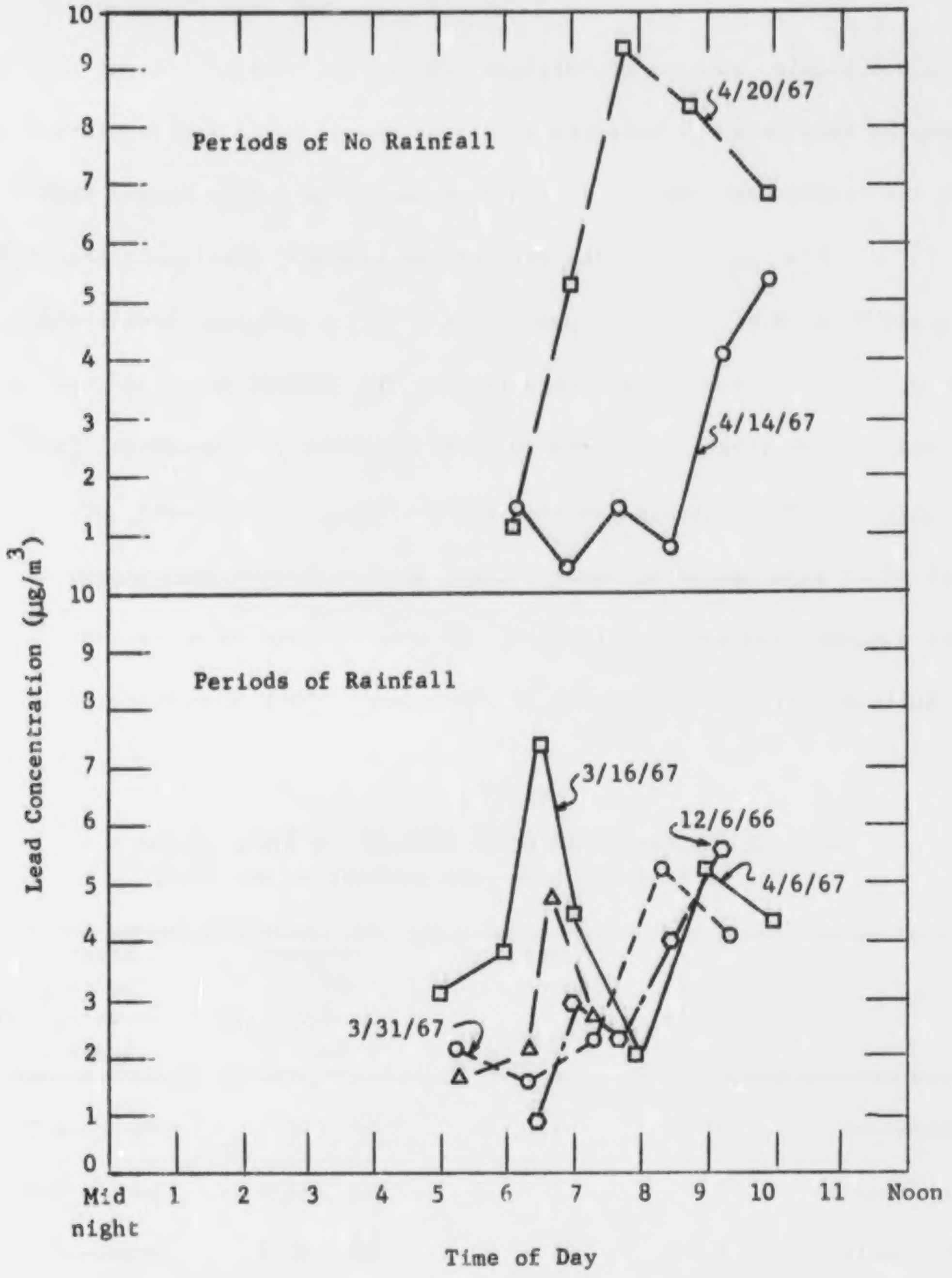


FIGURE 5-7
ATMOSPHERIC LEAD CONCENTRATION -- FREEWAY SITE, WINTER AND SPRING

the Los Angeles suburbs of Pasadena and Vernon. Three to eight hour samples were taken at selected locations chosen to be representative of the surrounding areas. In San Francisco, the levels ranged from 1.13 to 4.43 $\mu g/m^3$. In the city of Los Angeles, the levels observed ranged from 2.91 to 15.4 $\mu g/m^3$; and, in the suburbs, levels ranging from 2.33 to 4.42 $\mu g/m^3$ were found. The Working Group on Lead Contamination (1965) monitored 20 sampling sites in Cincinnati, Los Angeles and Philadelphia for one year to determine the levels of pollution experienced by those cities, and to observe the changes in the average lead levels throughout the year. Their airborne lead results are briefly summarized in Table 5-1. They also reported that

TABLE 5-1

AVERAGE AIRBORNE LEAD CONCENTRATION IN THREE CITIES
(The Working Group on Lead Contamination, 1965)

City	Number of Sites	Average Concentration ($\mu g/m^3$)	Highest Monthly Concentration ($\mu g/m^3$)	Lowest Monthly Concentration ($\mu g/m^3$)
Cincinnati	4	1.4	Oct.--2.1	March--0.9
Los Angeles	8	2.5	Dec.--3.9	June --1.7
Philadelphia	8	1.6	Oct.--2.3	March--1.2

three hour samples taken from a mobile sampler in heavy traffic indicate average lead concentrations ranging from 7.0 to 26.7 $\mu g/m^3$ in Cincinnati, and 4.5 to 71.3 $\mu g/m^3$ in Los Angeles. The mean values observed by the mobile unit on the freeway were similar to those obtained from samplers placed on the shoulder of a major freeway in Los Angeles.

Other values of airborne lead concentrations have been reported, but correlation of the data is difficult, since the pollution levels reported are strongly dependent on the sampler locations, atmospheric conditions and traffic patterns.

These air sample data indicate that the maximum lead pollution occurs at or near a major freeway. This contamination is of interest because the higher lead levels observed here may be hazardous to those using the freeway, or living near the freeway (Goldsmith, 1967). In addition, the concentrations at the freeway sampling site are indicative of the strength of the freeway as a source of lead pollution. For convenience and brevity in the following presentation, the traffic patterns which normally occur during weekdays can be divided into four classes:

CLASS I: Very low density, high speed traffic (< 25 vehicles/minute); midnight to 5:00 a.m.

CLASS II: High density, moderate speed, morning rush traffic (50 - 200 vehicles/minute); 5:30 a.m. to 9:30 a.m.

CLASS III: Moderate density, high speed, mid-day traffic (75 - 100 vehicles/minute); 9:30 a.m. to 3:00 p.m. and 6:30 p.m. to midnight.

CLASS IV: Very high density, low speed (often stop-start) evening rush traffic (100 - 200 vehicles/minute); 3:00 p.m. to 6:30 p.m.

Figures 5-1 through 5-6 show that the lead concentration in the atmosphere at the freeway followed a diurnal pattern, with peak levels occurring in the morning and late afternoon. In the early morning hours (Class I traffic) the atmosphere at the freeway contained small amounts of lead (usually less than 2 $\mu g/m^3$). These low concentrations can probably be considered as background levels for the area. During the morning rush period (Class II traffic), the lead concentrations closely paralleled the traffic flow, usually reaching a maximum level between 7:30 and 8:30 a.m. The peak traffic flow of 150 - 200 vehicles/minute consistently occurred at approximately 7:45 a.m. During the Class III traffic period, the lead concentration was more nearly constant, as was the traffic flow (75 - 90 vehicles/minute). The average concentration during this period was usually less than one-half the peak level reached during the morning rush period. A second peak in lead concentration occurred during the Class IV traffic period, but this peak value was normally much less than the morning peak, even though the traffic flow was greater during the evening rush.

During the morning hours, when little atmospheric mixing occurred because of low wind velocity and a nocturnal inversion which often persisted until mid-morning, the atmospheric lead concentrations observed at the freeway seemed to correlate well with the traffic flow. Figure 5-8 is a plot of the lead concentrations and corresponding traffic flows during periods of Class I, II, and III traffic when no winds were observed. With the exception of five of the data points, which showed unusually low lead concentrations, the data seemed to fall along a linear curve. The lower lead levels indicate that increased mixing and dilution occurred during these sampling periods. However, in order to estimate the maximum lead concentrations to be expected for given traffic flows, these lower data points were ignored, and a least squares linear fit was determined for the remaining 37 points. The resulting curve can be described by

$$L = 0.6 + 0.09F$$

where

L = lead concentration ($\mu g/m^3$)

F = traffic flow (vehicles/minute)

The standard deviation of these data from the line was found to be $\pm 2.1\ \mu g/m^3$.

In order to determine what portion of the total particulate loading of the atmosphere was composed of lead pollutants, longer air samples were taken (1, 12, or 24 hours). These data are given in Table 5-2. The total particulate loading and the percentage of lead present was highest near the freeway. The average particulate concentration ranged from 130 to 230 $\mu g/m^3$ and the average lead concentrations ranged from 5.8 to 14 $\mu g/m^3$. The highest percentage was observed in a one hour sample taken during the morning rush period, when ten percent of the mass of the airborne particulate matter was lead. The average percentage observed in consecutive 12 hour samples was 4.2 ± 1.2%. The percentage of lead decreased with distance from the freeway, but even at the foothills site, five miles away, 1.6 ± 0.1% of the total mass of suspended matter was lead. The 12 hour samples collected at the residential site contained 1.8 ± 0.2% lead.

These data compare favorably with the values found in Cincinnati, Los Angeles and Philadelphia in 1961 and 1962 by the Working Group on Lead Contamination (1965). In Cincinnati, an average of 1.7% of the particulate matter was lead; in Los Angeles 2.3% was lead and in Philadelphia 1.5% was lead. The highest percentages were observed in the late fall and the lowest in the spring or early summer. In Los Angeles, where the climate is similar to the climate in the Palo Alto area, the average amount of lead in airborne particulate matter reached

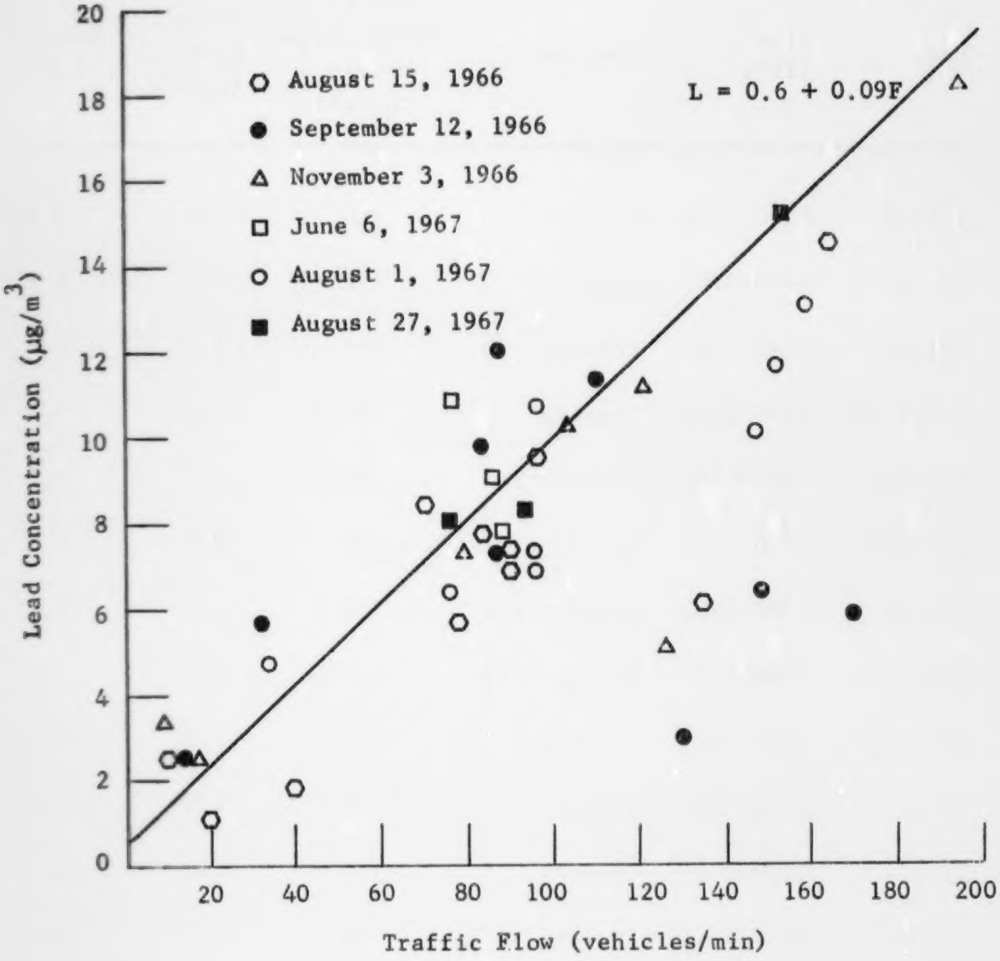


FIGURE 5-8
LEAD CONCENTRATION IN THE ATMOSPHERE AS
A FUNCTION OF TRAFFIC FLOW - FREEWAY SITE
(Periods of No Wind)

TABLE 5-2

LEAD AND TOTAL PARTICULATE MATTER IN AIR SAMPLES

Date	Time (PST)	Location	Total Particulate Matter ($\mu g/m^3$)	Total Lead ($\mu g/m^3$)	Percent Lead
1/7/68	0700-1900	Freeway	150	5.8	3.9
1/7,8/68	1900-0700	Freeway	230	7.6	3.3
1/8/68	0700-1900	Freeway	150	9.5	6.2
1/8,9/68	1900-0700	Freeway	170	6.2	3.5
1/7/68	0700-1900	Residential	100	2.1	2.1
1/7,8/68	1900-0700	Residential	150	2.9	1.9
1/8/68	0700-1900	Residential	100	1.6	1.6
1/8,9/68	1900-0700	Residential	140	2.4	1.7
1/7,8/68	0700-0700	Foothill	120	1.8	1.5
1/8,9/68	0700-0700	Foothill	110	2.0	1.8
8/1/67	0900-0955	Freeway	160	6.6	4.1
11/3/66	0800-0845	Freeway	140	14.0	10.0
11/3/66	1145-1245	Freeway	170	7.0	4.2
11/3/66	1645-1745	Freeway	130	6.2	4.8

3.7% in December and decreased to a low of 1.2% in June. Similarly, Mueller et al. (1963) reported that during 1954 and 1955, an average of 3.4% of the particulate matter in Berkeley, California was lead; and Lee et al. (1968) reported that 1.5% of the particulate matter over Fairfax, a Cincinnati suburb, was lead.

The Andersen Sampler was used to conduct three lead aerosol size measurements at the freeway site during the morning rush period. These tests were conducted to obtain a general idea of the size of the particles with which the lead contaminants were associated. Two samples were taken on August 1, 1967 when light to moderate winds (less than three miles per hour) were blowing and a third was taken the following week when a stronger wind was blowing. The particle size calculations were made according to the procedure outlined on page 66, Chapter 4, again assuming an average particle density of $5.85\ g/cm^3$ (density of $PbCl_2$). The results of these measurements are given in Table 5-3 and the resulting size distributions are plotted in Figure 5-9.

The two samples obtained on the first day are similar, each having a mass median diameter of approximately 1.0 microns. The third sample, taken the following week, contained more small particles, exhibiting a mass median diameter of 0.4 micron. This reduction in the mass median diameter is probably due, at least in part, to the

TABLE 5-3

AEROSOL SIZE DISTRIBUTIONS - FREEWAY SITE

Andersen Sampler Stage	Cut-off Diameter (μ)	Amount of Lead Collected (μg)	Percent of Total Sample (%)	Cummulative Percent
Test #1 - 50 ft^3 = 1.39 m^3 Light Winds - 0715-0805 June 9, 1967				
1	3.25	6.0	29.5	29.5
2	2.14	2.7	13.3	42.8
3	1.14	0.9	4.4	47.2
4	0.66	1.3	6.6	53.8
5	0.31	2.8	13.6	67.4
6	0.16	3.6	17.7	85.1
Clean-Up Filter		3.0	14.9	100.0
		18.3	100.0	
Average Concentration	$\frac{18.3\ \mu g}{1.39\ m^3} = 13.2\ \mu g/m^3$			
Test #2 - 60 ft^3 = 1.66 m^3 Light - Moderate Winds - 0915-1015 June 9, 1967				
1	3.25	2.4	21.9	21.9
2	2.14	1.3	12.2	34.1
3	1.14	1.6	15.0	49.0
4	0.66	0.9	8.1	57.2
5	0.31	0.9	8.1	65.3
6	0.16	1.8	16.3	81.6
Clean-Up Filter		1.9	18.4	100.0
		10.8	100.0	
Average Concentration	$\frac{10.8\ \mu g}{1.66\ m^3} = 6.5\ \mu g/m^3$			

TABLE 5-3, Continued

Andersen Sampler Stage	Cut-off Diameter (μ)	Amount of Lead Collected (μg)	Percent of Total Sample (%)	Cummulative Percent
		Test #3 - 75 ft^3 = 2.02 m^3 Windy - 0745-0900 June 16, 1967		
1	3.25	2.2	12.0	12.0
2	2.14	1.8	9.6	21.6
3	1.14	1.3	6.8	28.4
4	0.66	2.5	13.2	41.6
5	0.31	2.7	14.0	55.6
6	0.16	2.3	12.4	68.0
Clean-Up Filter		6.0	32.0	100.0
		18.8	100.0	

Average Concentration $\frac{18.8\ \mu g}{2.02\ m^3} = 9.3\ \mu g/m^3$

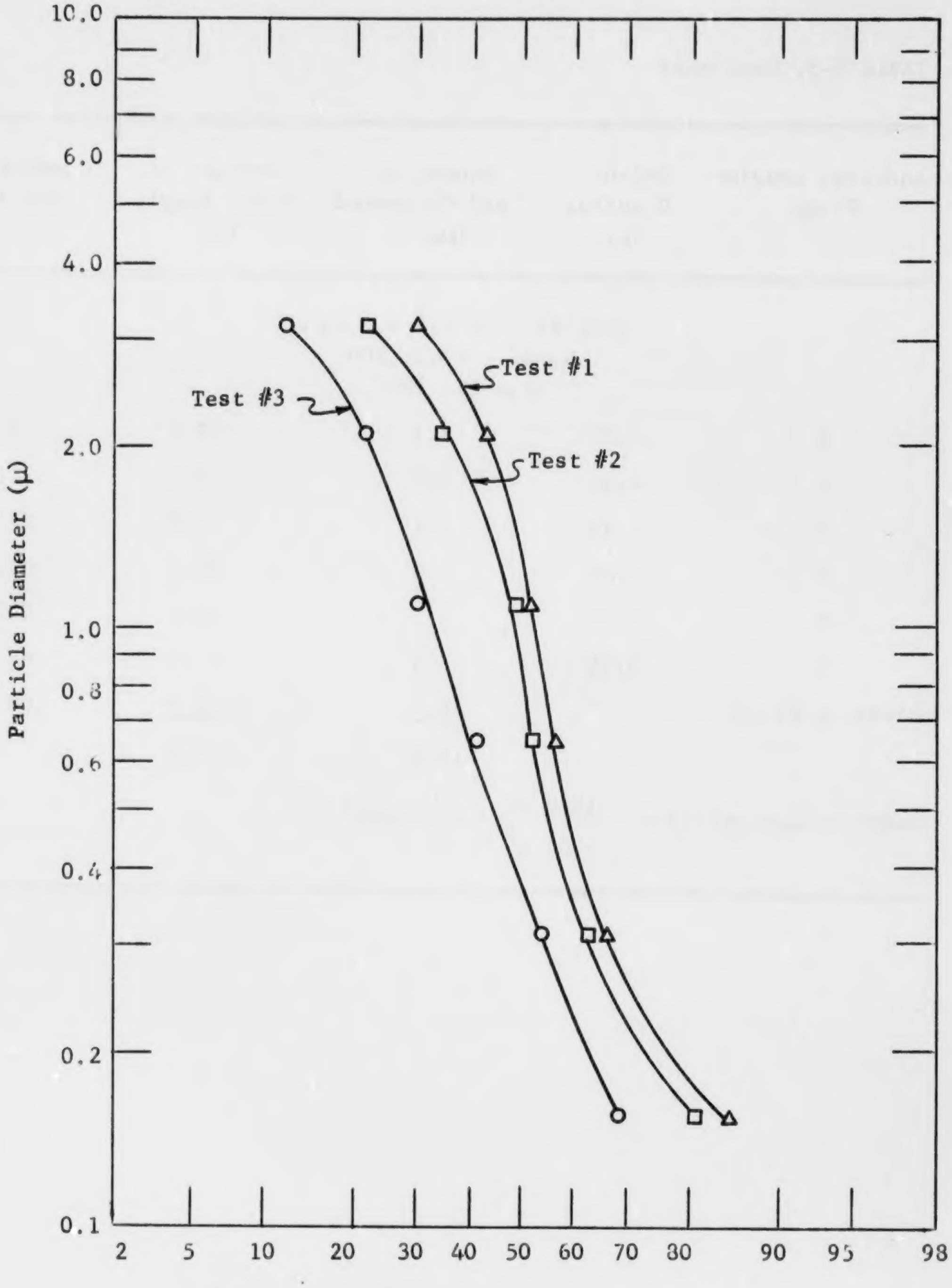


FIGURE 5-9
AEROSOL SIZE DISTRIBUTION TESTS -- FREEWAY SITE

increased wind velocity during Test #3. These few data do not allow a definitive size distribution to be determined, but they do show that the lead present in the atmosphere near the freeway is associated with small particulate matter. The mass median diameters obtained in these tests are considerably larger than those reported recently by Robinson (1964) and Lee et al. (1968), and slightly smaller than those reported by Tufts (1959).

2. Dry Sedimentation

The effectiveness of dry sedimentation as a removal process for lead pollutants was observed by collecting weekly dry fallout samples at the three sites. The mass of non-volatile solids (NVS) and the amount of total lead and soluble lead were determined each week and the data are given in Table 5-4. Easily detectable quantities of lead and non-volatile solids were collected at all the sites. The major source of error in the dry fallout program was in obtaining a representative aliquot from each sample for analysis. Each sample bag was vigorously shaken and the aliquots were withdrawn from the center of the sample. The aliquots chosen were as large as could be conveniently analyzed. Check tests were run on some samples and it was found that sampling errors were relatively small, usually within 5%.

Even though the amount of lead pollutants produced in the area was relatively constant from week to week (uniform traffic flow and

TABLE 5-4

WEEKLY DRY FALLOUT DATA -- ONE SQUARE FOOT COLLECTORS

	Freeway			Residential			Foothills		
Week Ending	NVS (mg)	Total Lead (mg)	Soluble Lead (mg)	NVS (mg)	Total Lead (mg)	Soluble Lead (mg)	NVS (mg)	Total Lead (mg)	Soluble Lead (mg)
5/21/67	197	1.25	0.084						
5/29/67	90	0.69	0.024						
6/9/67	73	0.66	0.028						
6/16/67	65	0.73	0.062						
6/23/67	15	0.33	0.050						
7/2/67	40	0.70	0.016						
7/11/67	40	0.70	0.016						
7/18/67	61	0.18	0.031				3	0.075	0.020
7/25/67	84	1.14	0.042				80	0.315	0.018
8/1/67	114	0.33	0.046				82	0.192	0.030
8/8/67	96	0.88	0.013				61	0.220	0.050
8/15/67	153	2.25	0.049				40	0.330	0.132
8/22/67	110	1.73	0.051				102	0.380	0.031
8/29/67	113	2.18	0.047				76	0.270	0.060
9/5/67	150	2.18	0.020				58		
8/12/67	118	1.08	0.230				77	0.157	0.036
9/19/67	70	0.93	0.052				80	0.180	0.018
9/26/67	99	1.15	0.025				28	0.063	0.007

TABLE 5-4, Continued

	Freeway			Residential			Foothills		
Week Ending	NVS (mg)	Total Lead (mg)	Soluble Lead (mg)	NVS (mg)	Total Lead (mg)	Soluble Lead (mg)	NVS (mg)	Total Lead (mg)	Soluble Lead (mg)
10/3/67	89	0.83	0.067				109	0.195	0.034
10/10/67	71	0.56	0.018	13	0.165	0.026	79	0.135	0.027
10/17/67	58	0.57	0.036	12	0.155	0.038	44	0.108	0.061
10/24/67	60	0.56	0.018	32	0.270	0.035	47	0.106	0.033
10/31/67	55	0.56	0.024	42	0.327	0.034	155	0.179	0.040
11/7/67	73	1.18	0.078	29	0.312	0.024	79	0.173	0.026
11/14/67	90	0.89	0.052	10	0.190	0.024	71	0.197	0.092
11/21/67	57	0.56	0.027	27	0.705	0.021	40	0.156	0.056
11/28/67	135	0.95	0.022	23	0.248	0.020	34	0.150	0.038
12/5/67				26	0.078	0.016			
12/12/67	82	0.59		15	0.177		32	0.072	
12/19/67	40	0.95	0.050	19	0.177	0.013			
12/26/67	29	0.54	0.033	12	0.196	0.034	7	0.064	0.025
1/2/68	30	0.45	0.045	25	0.233	0.027	5	0.036	0.012
1/9/68	73	0.88	0.100	23	0.300	0.022	74	0.133	0.013
1/16/68	158	2.06	0.178	3	0.071	0.006	40	0.277	0.052
1/23/68	65	0.85	0.011	41	0.466	0.041	12	0.097	0.022
1/30/68	177	1.18	0.105	29	0.320	0.049	120	0.230	0.055

TABLE 5-4, Continued

Week Ending	Freeway NVS (mg)	Freeway Total Lead (mg)	Freeway Soluble Lead (mg)	Residential NVS (mg)	Residential Total Lead (mg)	Residential Soluble Lead (mg)	Foothills NVS (mg)	Foothills Total Lead (mg)	Foothills Soluble Lead (mg)
2/7/68	270	2.00	0.054	17	0.174	0.005	12	0.180	0.036
2/14/68	103	0.99	0.015	16	0.175	0.013	5	0.099	0.036
2/21/68	44	0.43	0.026	11	0.165	0.012	45	0.166	0.027
2/28/68	71	0.65	0.019	31	0.222	0.016	17	0.131	0.020
3/6/68	82	0.65	0.028	28	0.209	0.018	28	0.145	0.021
3/13/68	225	1.40	0.100	37	0.230	0.030	100	0.150	0.054
3/20/68	250	1.63	0.098	31	0.162	0.008	72	0.168	0.038
3/27/68	125	0.50	0.020	68	0.230	0.013	20	0.054	0.008
4/3/68	207	0.65	0.051	45	0.222	0.023	35	0.108	0.043
4/10/68	82	0.60	0.033	20	0.129	0.014	7	0.081	0.017
4/17/68	132	0.98	0.165	32	0.174	0.020	28	0.126	0.055
4/24/68	96	0.55	0.080	51	0.276	0.015	45	0.174	0.027
5/1/68	79	0.97	0.140	36	0.273	0.025	29	0.125	0.070
5/8/68	119	0.82	0.075	44	0.221	0.021	40	0.083	0.017
5/15/68	147	0.54	0.290	54	0.300	0.170	45	0.135	0.042
5/22/68	47	0.55	0.032	46	0.240	0.020	24	0.072	0.008
5/29/68	89	0.74	0.035	64	0.394	0.070	29	0.084	0.014
6/4/68	71	0.87	0.052	42	0.300	0.038	20	0.088	0.028
AVERAGE	98	0.92	0.060	26	0.241	0.029	52	0.153	0.038

industrial activity), large fluctuations were observed in the amount of lead in dry fallout. The extent of the fluctuations can be seen in Figure 5-10, a plot of the weekly dry fallout data at the three sites. The data were assumed to be normally distributed and the means and standard deviations were calculated. These results are summarized in Table 5-5.

The average values shown in Table 5-5 indicate that the amount of lead present in dry fallout decreased rapidly with distance from the freeway. If it is assumed that the average values obtained at the three points are a part of a continuous curve relating average lead fallout to distance from the freeway, simple curve fitting techniques can be used to determine the form of an expression and the parameters which will define the relationship.

Figure 5-11 is a semi-log plot of the three average lead values as a function of distance from the freeway. The data appear to fall along a straight line, suggesting that the relationship between lead in fallout, L, and distance from the freeway, X, can be described by

$$X = ae^{bL}$$

where a and b are constants.

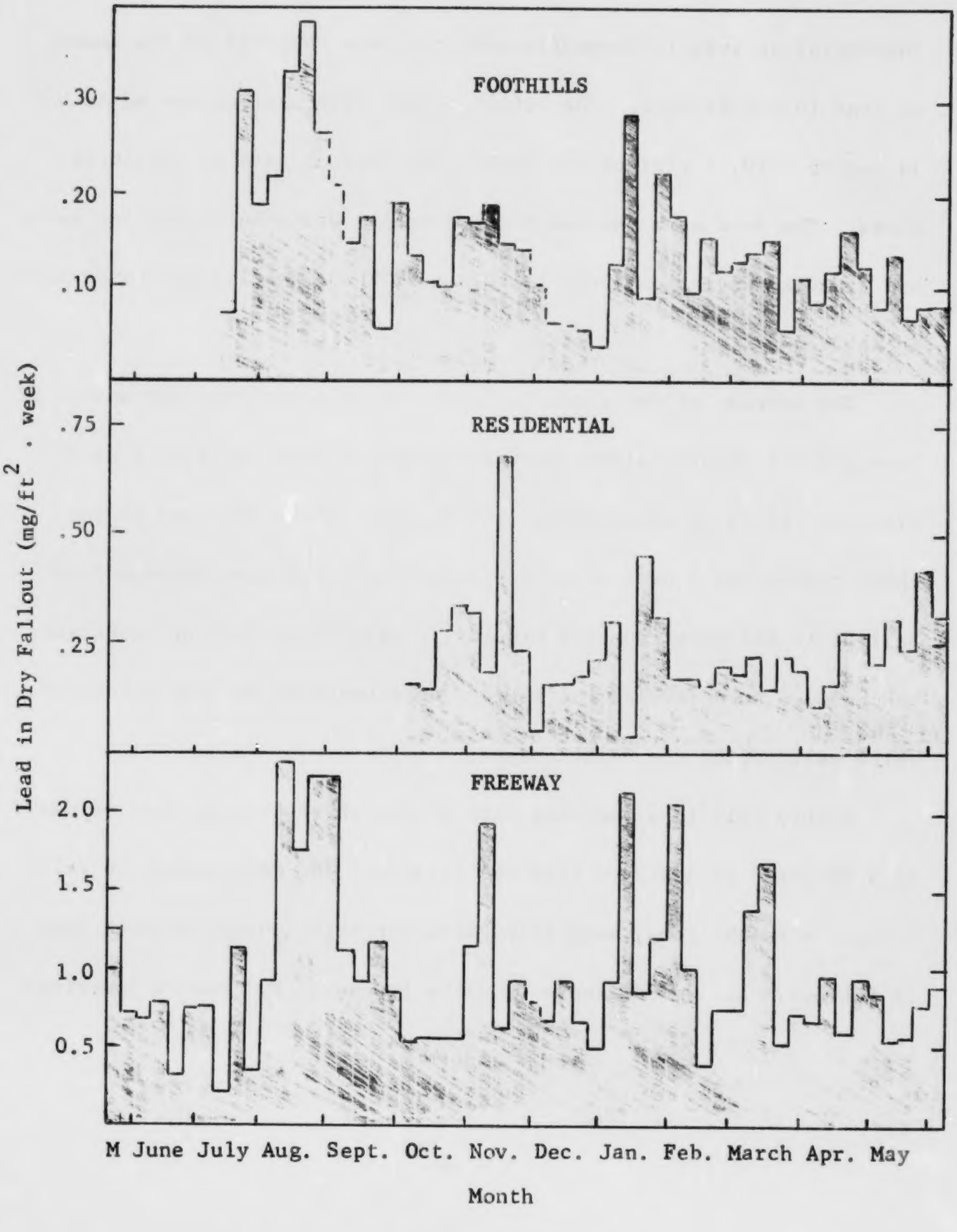


FIGURE 5-10
TOTAL LEAD IN WEEKLY DRY FALLOUT SAMPLES -- THREE LOCATIONS

TABLE 5-5

DRY FALLOUT DATA -- SUMMARY

	Location		
	Freeway	Residential	Foothills
Distance from Freeway - feet	50	12,600	26,900
Average NVS $mg/ft^2 \cdot wk$	98	26	52
Standard Deviation	20	14	9
Average Lead $mg/ft^2 \cdot wk$	0.92	0.24	0.15
Standard Deviation	0.23	0.12	0.07
Maximum Lead Collected $mg/ft^2 \cdot wk$	2.18	0.70	0.38
Minimum Lead Collected $mg/ft^2 \cdot wk$	0.18	0.07	0.04
Average Soluble Lead $mg/ft^2 \cdot wk$	0.06	0.03	0.04
Standard Deviation	0.05	0.02	0.02

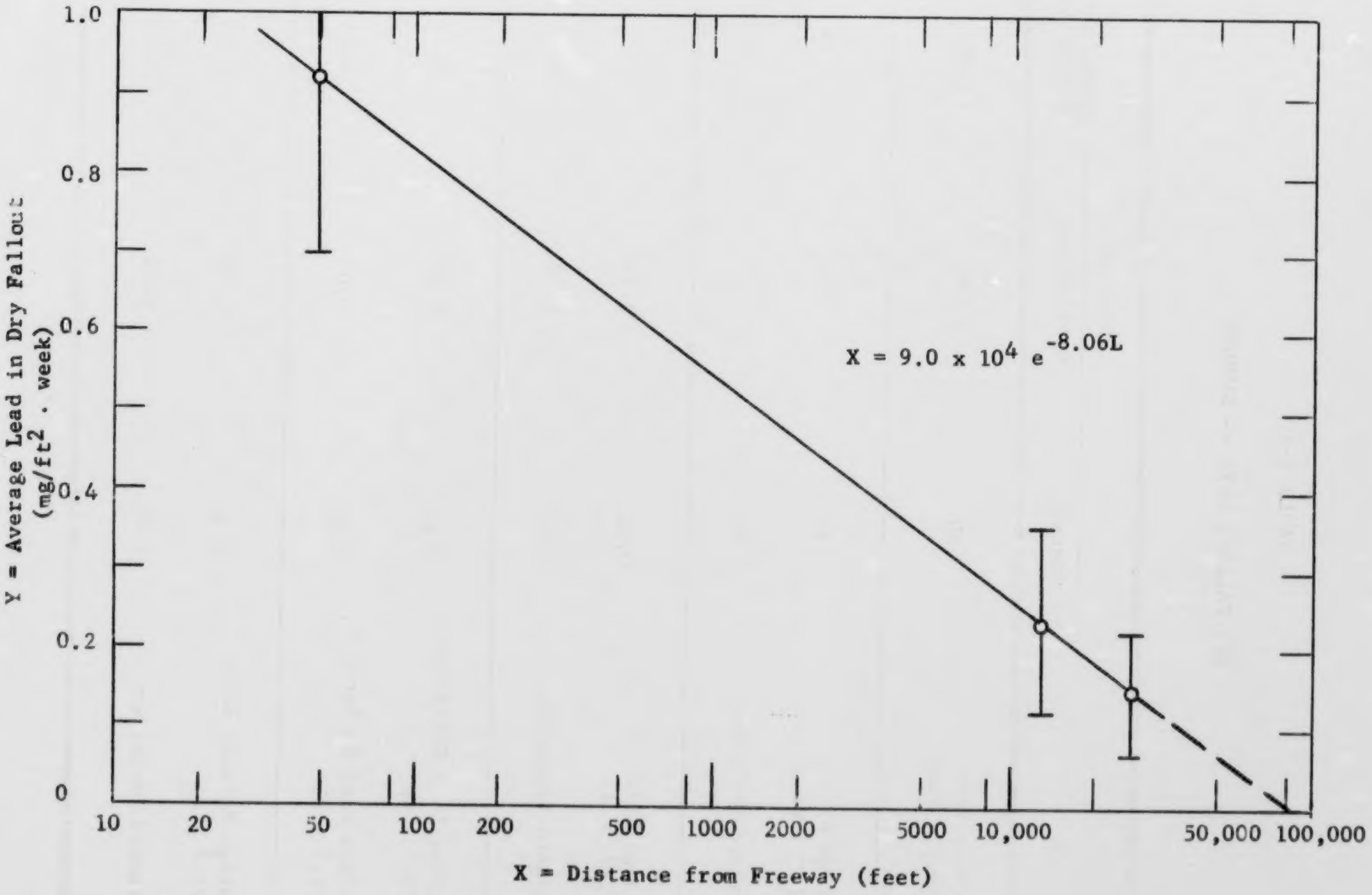


FIGURE 5-11
AVERAGE LEAD IN DRY FALLOUT AS A FUNCTION OF DISTANCE FROM THE FREEWAY

From the semi-log plot, the appropriate values for a and b are

$$a = 9.0 \times 10^4$$

$$b = -8.06,$$

if L is expressed in $mg/ft^2 \cdot wk$ and X is expressed in feet. Therefore

$$X = 9.0 \times 10^4 e^{-8.06L}$$

The area under this curve, from $X_1 = 50'$ to $X_3 = 26{,}900'$, should represent the total amount of lead deposited in the Palo Alto area for each one foot section of freeway. This value is 7.85 g/ft. The area under the curve from $L = 0.95\ mg/ft^2 \cdot wk$ to $L = 0$ should represent the total amount of lead that was removed by sedimentation, assuming that the data can be extrapolated past 26,900 feet. This value is 11.1 g/ft. This indicates that an average of 70% of the lead which was removed by sedimentation was removed within five miles of the source.

Traffic counts showed that, during the sampling period, approximately 650,000 vehicles used the Bayshore Freeway each week in the

Palo Alto area. Since each car averages 15 miles per gallon of fuel (Panel on Electrically Powered Vehicles, 1967), the total amount of lead exhausted in the one foot section considered above can be estimated by

Lead Conc. x gasoline consumed per foot x no. of automobiles = lead consumed

$$2\ \text{g/gal} \times 1/15\ \frac{\text{gallon}}{\text{mile}\cdot\text{vehicle}} \times \frac{1\ \text{mile}}{5280\ \text{ft.}} \times 650{,}000\ \frac{\text{vehicle}}{\text{week}} = 16.4\ \text{g/wk}\cdot\text{ft}$$

$$(16.4\ \text{g/wk}\cdot\text{ft}) \times .80\ (\text{fraction exhausted}) = 13.1\ \text{g/ft}\cdot\text{wk}$$

Thus, an average of 13.1 g/ft of lead was produced by the freeway traffic and 7.85 g/ft was present in dry fallout. Assuming no contribution to the dry fallout samples from local traffic, dry sedimentation accounted for the removal of approximately 60% of the lead pollutants within five miles of the source. If it is assumed that 20% of the lead in fallout at the residential and foothills sites was due to local traffic, similar calculations indicate that 38% of the lead exhausted at the freeway was removed by sedimentation within five miles of the source. However, the relatively low traffic volumes and the small amounts of lead exhausted at city driving speeds, suggest that local traffic in the Palo Alto area contributed little to the lead in fallout.

The lead which was collected in dry fallout appears to have been associated with the dustfall at the collection sites. Figures 5-12 and 5-13 are plots of the total lead in the dry fallout as a function of the non-volatile solids collected each week. The data indicate that the lead to dustfall relationships at the collection sites may be approximated by linear curves. The slope of the curve which best fits the data obtained at the freeway is 0.014 milligrams of lead per milligram of non-volatile solids; the slope of the best curve for the residential data is 0.005 milligrams of lead per milligram of non-volatile solids; and the slope of the best curve for the foothills data is 0.002 milligrams of lead per milligram of non-volatile solids. Cholak (1961) reported that the soil in North and South America contains an average of 0.000034 milligrams of lead per milligram of soil, and that values as high as 0.00036 milligrams of lead per milligram of soil have been found in older areas in Cincinnati. DeTreville (1964) reported similar values. Thus, it would appear that the fraction of lead in soil is much less than that in dry fallout.

The five sample points collected at the freeway site during weeks when heavy rainfall occurred, and indicated in Figure 5-12 by the symbol ☐ , contained large amounts of non-volatile solids, probably

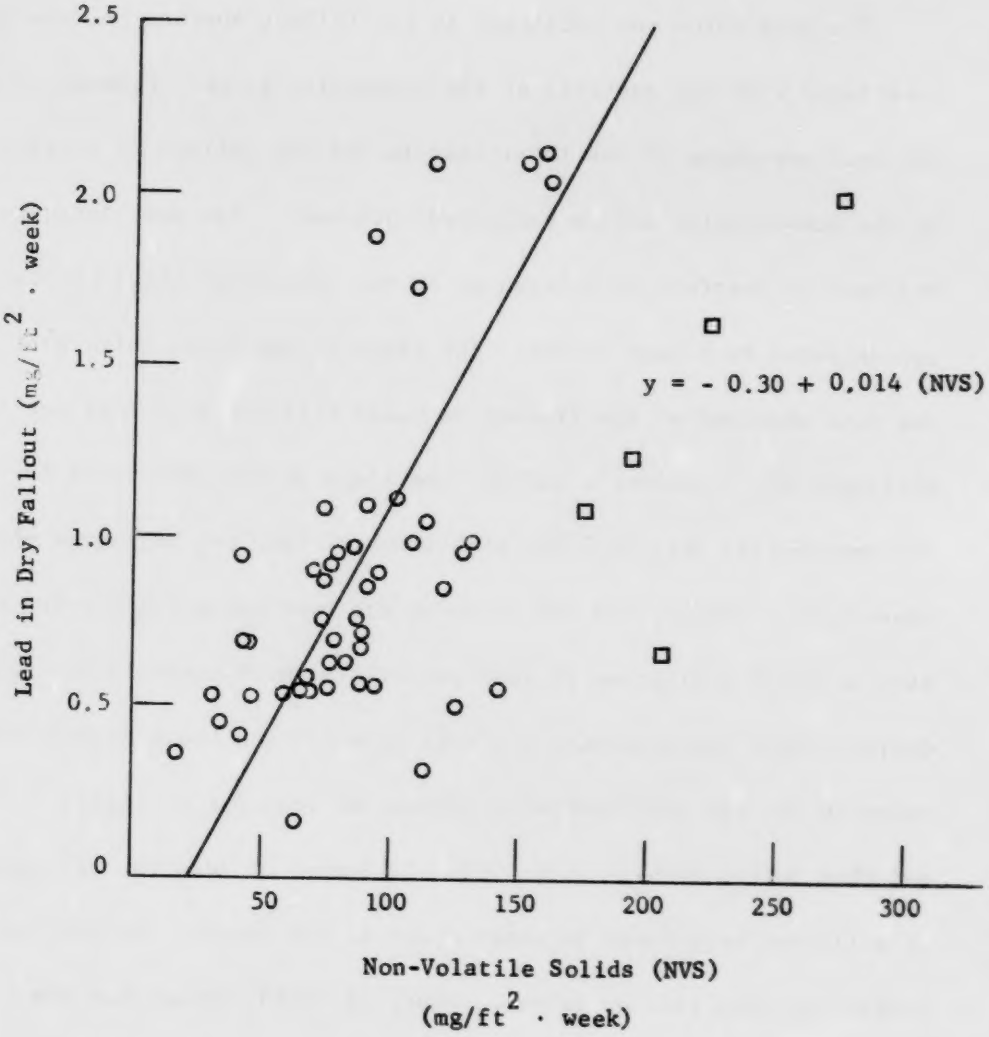


FIGURE 5-12
LEAD AND NON-VOLATILE SOLIDS IN DRY FALLOUT AT THE FREEWAY SITE

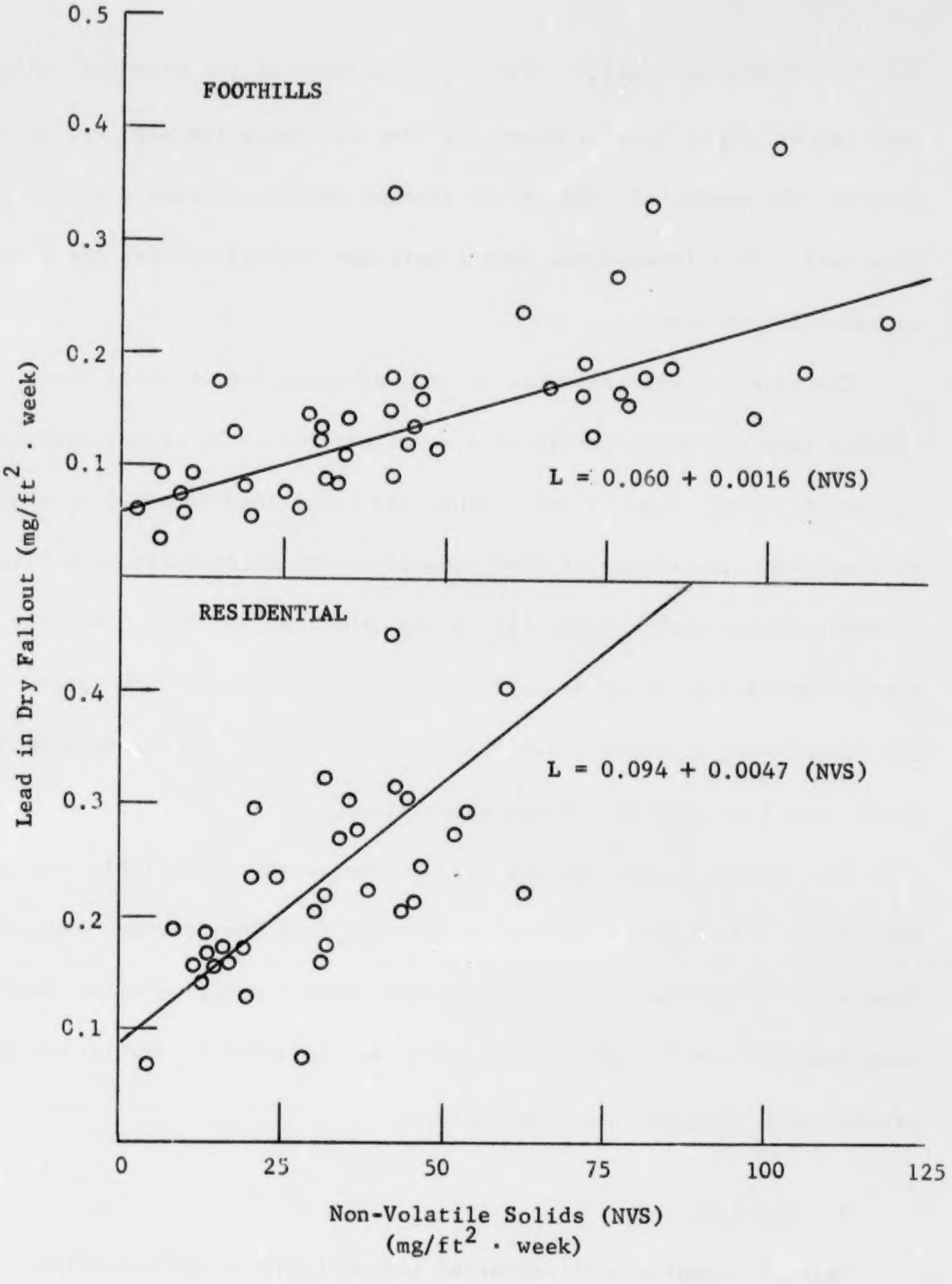


FIGURE 5-13
LEAD AND NON-VOLATILE SOLIDS IN DRY FALLOUT
FOOTHILLS AND RESIDENTIAL SITES

due to raindrop scavaging. However, since much of the raindrop scavaging occurred at higher levels, where the lead contamination was considerably reduced, the amount of lead in the samples was not increased proportionately. Therefore, these points were not considered when the line of best fit was drawn.

The relative effectiveness of dry sedimentation on total lead, soluble lead and non-volatile solids was determined by calculating the ratios of soluble lead to total lead, and total lead to total non-volatile solids. The ratios of lead removal at the three sites were also calculated each week. These ratios are contained in Table 5-6. The mean values and standard deviations were calculated for each ratio, and the results are given in Table 5-7. In most cases, the standard deviations were less than 50% of the mean values.

The average ratios suggest that the percentage of soluble lead in dry fallout increased rapidly with distance from the freeway. Near the freeway, 6.6% of the lead in fallout was soluble and, five miles away, more than 24% was soluble. The lead to non-volatile solids ratios decreased with distance from the freeway.

3. Rainfall

Rainfall samples were collected and analyzed to determine how effectively lead particulate matter was removed by the washout and rainout processes. Northern California has a Mediterranean-type

TABLE 5-6

WEEKLY DRY FALLOUT DATA RATIOS

	Soluble Lead/Total Lead			Total Lead/Non-Volatile Solids			Total Lead Ratios		
Week Ending	Freeway	Residential	Foothills	Freeway	Residential	Foothills	Freeway / Residential	Freeway / Hills	Residential / Hills
5/21/67	0.067			0.0063					
5/29/67	0.035			0.0077					
6/9/67	0.042			0.0090					
6/16/67	0.085			0.0012					
6/23/67	0.155			0.0210					
7/2/67	0.020			0.0175					
7/11/67	0.020			0.0175					
7/18/67	0.170		0.260	0.0292		0.0250		2.4	
7/25/67	0.035		0.057	0.0136		0.0039		3.7	
8/1/67	0.030		0.160	0.0139		0.0023		8.2	
8/8/67	0.014		0.220	0.0091		0.0035		4.0	
8/15/67	0.020		0.400	0.0147		0.0082		6.8	
8/22/67	0.030		0.080	0.0157		0.0034		4.5	
8/29/67	0.020		0.220	0.0192		0.0035		8.1	
9/5/67	0.010			0.0145					
9/12/67	0.210		0.230	0.0091		0.0020		6.8	
9/19/67	0.056		0.100	0.0133		0.0022		5.1	
9/26/67	0.022		0.120	0.0116		0.0022		18.3	

TABLE 5-6, Continued

Week Ending	Soluble Lead/Total Lead			Total Lead/Non-Volatile Solids			Total Lead Ratios		
	Freeway	Residential	Foothills	Freeway	Residential	Foothills	Freeway / Residential	Freeway / Hills	Residential / Hills
10/3/67	0.080		0.180	0.0095		0.0018		4.3	
10/10/67	0.032	0.160	0.170	0.0079	0.0130	0.0017	3.4	4.2	1.2
10/17/67	0.063	0.240	0.560	0.0100	0.0130	0.0024	3.7	5.3	1.4
10/24/67	0.030	0.130	0.310	0.0106	0.0085	0.0023	2.1	5.3	2.5
10/31/67	0.043	0.100	0.220	0.0102	0.0078	0.0011	1.7	3.1	1.8
11/7/67	0.060	0.080	0.150	0.0160	0.0107	0.0025	3.8	6.8	1.8
11/14/67	0.060	0.120	0.480	0.0099	0.0190	0.0020	4.7	4.5	1.0
11/21/67	0.050	0.030	0.370	0.0098	0.0260	0.0039	0.8	3.6	4.5
11/28/67	0.230	0.081	0.220	0.0071	0.0108	0.0044	3.8	6.3	1.6
12/5/67	0.040	0.210	0.400						
12/12/67				0.0072	0.0118	0.0022	3.3	8.2	2.4
12/19/67	0.053	0.074	0.030	0.0240	0.0093	0.0028	5.4	4.9	
12/26/67	0.061	0.170	0.390	0.0186	0.0163	0.0091	2.8	8.4	3.0
1/2/68	0.100	0.120	0.330	0.0152	0.0093	0.0080	1.9	12.5	6.5
1/9/68	0.090	0.080	0.100	0.0143	0.0130	0.0018	2.9	6.6	2.2
1/16/68	0.087	0.085	0.190	0.0130	0.0236	0.0069	29.1	7.4	0.2
1/23/68	0.012	0.088	0.230	0.0131	0.0114	0.0076	1.8	8.8	4.7
1/30/68	0.090	0.150	0.240	0.0067	0.0111	0.0019	3.7	5.2	1.4
2/7/68	0.025	0.030	0.200	0.0074	0.0102	0.0150	11.5	11.1	1.0
2/14/68	0.015	0.075	0.360	0.0097	0.0109	0.0192	5.6	10.0	1.8
2/21/68	0.060	0.073	0.160	0.0098	0.0150	0.0037	2.6	2.6	1.0
2/28/68	0.030	0.072	0.150	0.0092	0.0072	0.0077	2.9	5.0	1.7

TABLE 5-6, Continued

Week Ending	Soluble Lead/Total Lead			Total Lead/Non-Volatile Solids			Total Lead Ratios		
	Freeway	Residential	Foothills	Freeway	Residential	Foothills	Freeway / Residential	Freeway / Hills	Residential / Hills
3/6/68	0.042	0.086	0.140	0.0079	0.0074	0.0052	3.1	4.5	1.4
3/13/68	0.070	0.130	0.360	0.0064	0.0062	0.0015	6.1	9.4	1.5
3/20/68	0.060	0.050	0.220	0.0065	0.0052	0.0024	10.0	9.7	1.0
3/27/68	0.040	0.057	0.150	0.0040	0.0034	0.0027	2.2	9.2	4.2
4/3/68	0.078	0.100	0.400	0.0032	0.0049	0.0031	2.9	6.0	2.0
4/10/68	0.055	0.110	0.210	0.0073	0.0063	0.0115	4.6	7.4	1.6
4/17/68	0.170	0.120	0.440	0.0074	0.0054	0.0045	5.5	7.7	1.4
4/24/68	0.145	0.054	0.160	0.0057	0.0054	0.0039	2.0	3.2	1.6
5/1/68	0.140	0.091	0.570	0.0122	0.0077	0.0043	3.5	7.7	2.2
5/8/68	0.091	0.074	0.310	0.0069	0.0050	0.0021	3.7	9.9	2.6
5/15/68	0.230	0.057	0.200	0.0037	0.0055	0.0030	1.8	4.0	2.2
5/22/68	0.058	0.083	0.110	0.0116	0.0052	0.0030	2.3	7.6	3.3
5/29/68	0.047	0.180	0.170	0.0082	0.0062	0.0029	1.9	8.8	4.7
AVERAGE	0.066	0.102	0.244	0.0112	0.0102	0.0049	4.5	6.8	1.8

TABLE 5-7

DRY FALLOUT RATIOS -- SUMMARY

Ratio	Location		
	Freeway	Residential	Foothills
Average $\frac{\text{Soluble Lead}}{\text{Total Lead}}$	0.066	0.102	0.244
Standard Deviation	0.050	0.049	0.125
Average $\frac{\text{Total Lead}}{\text{NVS}}$	0.0112	0.0102	0.0049
Standard Deviation	0.0051	0.0045	0.0036
Average $\frac{\text{Lead At Freeway}}{\text{Lead At Other Sites}}$		4.5	6.8
Standard Deviation		2.2	3.0
Average $\frac{\text{Lead At Residential Site}}{\text{Lead At Foothills Site}}$			1.8
Standard Deviation			0.6

climate, with a rainfall season which usually begins in November and lasts until late March or early April. No significant precipitation occurs during the remainder of the year. A few exploratory rainfall samples were collected during the 1966-1967 season and samples of all rainfall were collected during the 1967-1968 season. The rainfall data are contained in Tables 5-8 through 5-11. The average lead concentrations were estimated by dividing the total lead collected by the total volume of rainfall collected. The concentrations found for each sample were not averaged because the sample volumes were not uniform. The results of the rainfall sampling program are summarized in Table 5-12. The major source of error in the rainfall program was in obtaining a representative aliquot from each sample for analysis. The samples were shaken vigorously and an aliquot was withdrawn from the center. Random check tests showed that the results obtained from duplicate analyses were within 8%.

The data indicate that the lead content of rainfall changed markedly from storm to storm and during a storm. Wide variations in other constituents during a storm have also been reported by Huff and Bradley (1965), Kruger (1966), and others. Since airborne lead particulate matter may be present in significant quantities near the surface and at higher levels, lead pollutants may enter rainfall by rainout and washout. Some of the factors which may affect the amount of lead

TABLE 5-8

EXPLORATORY RAINFALL SAMPLES - 1966-1967 SEASON

1 ft^2 Collectors

Date	Time (PST)	Volume (ml)	Freeway Pb Conc. (mg/l)	Hill Pb Conc. (mg/l)
11/15/66	0800	115	1.00	
	0900	75	0.540	
12/6/66	0615	180	0.433	
	0715	200	0.370	
	0815	90	0.367	
	0915	45	0.317	
3/16/67	0600	300	0.120	
	0630	650	0.044	
	0700	150	0.080	
4/6/67	0700	200	0.054	
	0730	620	0.067	
	0800	580	0.050	
	0830	500	0.050	
	0900	500	0.023	
	0930	200	0.063	0.062
4/10/67	0430	250	0.051	0.046
	0500	150	0.063	
	0530	150	0.071	
	1000	200	0.102	0.069
4/11/67	1200	650	0.100	0.043
4/14/67	0600	200	0.046	0.028
	1730	150	0.028	
4/15/67	0800	500	0.034	0.020
	1100	500	0.050	< 0.005

TABLE 5-8, Continued

			Freeway	Hill
Date	Time (PST)	Volume (ml)	Pb Conc. (mg/l)	Pb Conc. (mg/l)
4/17/67	1730	350	0.041	0.031
	2230	150	0.094	0.071
4/18/67	1100	450	0.086	0.031
	1730			0.023
4/19/67	1230	150	0.023	< 0.005
	1930	200	0.234	0.016
4/20/67	0600	100	0.291	
4/21/67	1100	1100	0.413	0.030
4/23/67	0800	700	0.135	0.120
4/25/67	0800	500	0.314	0.346

TABLE 5-9

LEAD IN RAINFALL -- FREEWAY SITE

1 ft^2 Collector

Date	Time (PST)	Volume (ml)	Total Conc. (mg/1)	Total Lead (mg)	Soluble Lead Concentration (mg/1)	Soluble Lead (mg)
11/7/67	0800	465	0.240	0.112		
11/27/67	1000	385	0.247	0.095		
11/29/67	1520	280	0.202	0.056	0.024	0.007
12/3/67	1800	275	0.204	0.056		
12/3/67	2100	370	0.180	0.067	0.044	0.016
12/5/67	0800	190	0.108	0.021		
12/6/67		420	0.252	0.106		
12/18/67	0800	445	0.540	0.250	0.196	0.088
12/19/67	0800	110	0.290	0.032	0.180	0.019
1/10/68		1270	0.246	0.312		
1/14/68	1000	200	0.500	0.100	0.024	0.004
1/14/68	1900	125	0.160	0.020	0.012	0.001
1/15/68	0700	200	0.500	0.100		
SUB-TOTAL		4735		1.327		0.135 (1530 ml)
AVERAGE CONCENTRATION			0.280		0.088	
1/29/68	1200	1000	0.156	0.156	0.018	0.018
1/30/68	0700	2425	0.027	0.067	0.013	0.031
1/30/68	1900	1700	0.044	0.075	< 0.005	0.007
2/20/68	0700	480	1.000	0.480	0.077	0.037
3/7/68	0800	1400	0.200	0.280	0.068	0.095
3/12/68	0700	1775	0.166	0.296	0.072	0.128
3/13/68	0800	590	0.150	0.089	0.093	0.055
3/15/68	1000	1150	0.062	0.071	0.052	0.060
3/16/68	1200	290	0.078	0.023	0.032	0.010
3/22/68	2100	450	0.123	0.055	0.090	0.040

TABLE 5-9, Continued

Date	Time (PST)	Volume (ml)	Total Conc. (mg/1)	Total Lead (mg)	Soluble Lead Concentration (mg/1)	Soluble Lead (mg)
4/1/68	0830	510	0.165	0.084	0.055	0.038
4/1/68	1800	460	0.078	0.036	0.039	0.023
SUB-TOTAL		12,230		1.712		0.542
AVERAGE CONCENTRATION			0.140		0.044	
TOTAL		16,965		3.039		
AVERAGE CONCENTRATION			0.180		0.056	

TABLE 5-10

LEAD IN RAINFALL -- RESIDENTIAL SITE

1 ft^2 Collector

Date	Time (PST)	Volume (ml)	Total Conc. (mg/1)	Total Lead (mg)	Soluble Lead Concentration (mg/1)	Soluble Lead (mg)
11/7/67	0030	100	0.399	0.040		
11/7/67	0800	275	0.102	0.028		
11/27/67	0800	500	0.192	0.096		
11/29/67	1450	220	0.162	0.036	0.042	0.008
11/29/67	1520	610	0.096	0.059	0.012	0.006
11/29/67	1645	310	0.060	0.018		
11/29/67	2115	60	0.144	0.008		
11/30/67	0645	370	0.114	0.042		
11/30/67	0745	130	0.057	0.007		
11/30/67	1400	320	0.444	0.142		
12/1/67	0800	170	0.114	0.020		
12/3/67	1800	320	0.505	0.164		
12/3/67	2100	660	0.192	0.127		
12/4/67	0800	120	0.136	0.043		
12/4/67	1900	210	0.240	0.050		
12/4/67	2200	420	0.080	0.034		
12/5/67	0200	150	0.138	0.021		
12/18/67	0800	1000	0.202	0.202	0.172	0.172
12/18/67	1800	270	0.260	0.070	0.072	0.020
12/18/67	2200	200	0.552	0.110	0.075	0.015
12/19/67	0800	240	0.182	0.045	0.072	0.017
1/10/68	0800	2000	0.125	0.250		
1/14/68	1000	170	0.210	0.044	0.000	0.000
1/14/68	1900	250	0.050	0.012	0.038	0.010
1/14/68	2200	550	0.072	0.040	0.030	0.015
1/15/68	0700	125	0.006	0.000	< 0.005	0.000
SUB-TOTAL		9750		1.708		0.263 (3635 ml)
AVERAGE CONCENTRATION			0.175		0.072	

TABLE 5-10, Continued

Date	Time (PST)	Volume (ml)	Total Conc. (mg/1)	Total Lead (mg)	Soluble Lead Concentration (mg/1)	Soluble Lead (mg)
1/26/68	2200	105	0.225	0.024	0.022	0.002
1/28/68	1000	530	0.260	0.135	0.018	0.010
1/29/68	1000	290	0.171	0.050	0.018	0.005
1/29/68	1200	120	0.135	0.016	0.015	0.002
1/29/68	2100	280	0.060	0.018	0.022	0.006
1/30/68	0400	2000	0.108	0.216	< 0.005	0.000
1/30/68	0430	160	0.075	0.012	< 0.005	0.000
1/30/68	0530	190	0.062	0.012	< 0.005	0.000
1/30/68	0700	425	0.020	0.008	< 0.005	0.000
1/30/68	0730	230	0.081	0.019	< 0.005	0.000
1/30/68	0900	170	0.046	0.008	0.024	0.004
1/30/68	1330	425	0.090	0.033	< 0.005	0.000
1/30/68	1530	420	0.075	0.032	< 0.005	0.000
1/30/68	1630	540	0.040	0.022	0.024	0.013
1/30/68	1930	675	0.030	0.020	< 0.005	0.000
2/16/68	0800	130	0.150	0.019	0.014	0.002
2/16/68	1000	230	0.210	0.048	0.018	0.004
2/19/68	1100	400	0.050	0.020	0.014	0.006
2/20/68	0700	440	0.216	0.090	0.020	0.008
3/6/68	0800	230	0.088	0.021	0.037	0.007
3/6/68	1800	260	0.380	0.099	0.014	0.004
3/7/68	0800	1200	0.200	0.240	0.021	0.025
3/12/68	1600	1100	0.100	0.220	0.060	0.066
3/12/68	1800	650	0.272	0.176	0.033	0.022
3/12/68	1900	320	0.260	0.083	0.024	0.008
3/12/68	2030	300	0.084	0.024	0.026	0.008
3/12/68	2130	360	0.190	0.068	0.051	0.018
3/12/68	2145	115	0.111	0.013	0.020	0.003
3/16/68	0600	355	0.070	0.025	0.060	0.020
3/16/68	0700	200	0.032	0.006	0.018	0.003
3/16/68	1500	200	0.070	0.014	0.060	0.012
3/22/68	2100	290	0.099	0.029	0.048	0.014

TABLE 5-10, Continued

Date	Time (PST)	Volume (ml)	Total Conc. (mg/l)	Total Lead (mg)	Soluble Lead Concentration (mg/l)	Soluble Lead (mg)
4/1/68	0800	400	0.226	0.091	0.051	0.020
4/1/68	0830	380	0.159	0.059	0.036	0.014
4/1/68	0900	360	0.138	0.050	0.033	0.012
4/1/68	1000	250	0.078	0.019	0.012	0.004
4/1/68	1300	260	0.045	0.011	0.012	0.004
4/1/68	1800	220	0.048	0.010	0.033	0.007
SUB-TOTAL		15,210		2.080		0.333
AVERAGE CONCENTRATION			0.133		0.022	
TOTAL		24,960		3.788		
AVERAGE CONCENTRATION			0.149		0.042	

TABLE 5-11

LEAD IN RAINFALL -- FOOTHILLS SITE

1 ft^2 Collector

Date	Time (PST)	Volume (ml)	Total Conc. (mg/1)	Total Lead (mg)	Soluble Lead Concentration (mg/1)	Soluble Lead (mg)
11/7/67	0800	300	0.070	0.021	0.061	0.018
11/27/67	0900	380	0.093	0.035	0.057	0.021
11/29/67	1520	600	0.068	0.041		
11/30/67	0745	560	0.051	0.029		
11/30/67	1400	575	0.063	0.036		
12/3/67	1800	300	0.098	0.030	0.054	0.016
12/3/67	2100	380	0.083	0.032	0.047	0.018
12/4/67	1000	600	0.031	0.019	0.012	0.007
12/5/67	0800	300	0.066	0.020	0.050	0.015
12/6/67	0800	200	0.132	0.026	0.062	0.012
12/18/67	0800	1150	0.066	0.076	0.054	0.062
12/19/67	0800	600	0.033	0.020	0.033	0.020
1/15/68	0700	1550	0.012	0.018	< 0.005	0.000
SUB-TOTAL		7495		0.403		0.189 (5760 ml)
AVERAGE CONCENTRATION			0.053		0.033	
1/29/68	1200	1440	0.019	0.027	0.015	0.022
1/30/68	0900	4850	0.011	0.053	0.009	0.044
2/20/68	0700	1210	0.032	0.039	0.022	0.027
3/7/68	0800	1525	0.043	0.065	0.020	0.030
3/12/68	0800	3500	0.050	0.175	0.022	0.078
3/16/68	1500	1525	0.052	0.080	0.018	0.027
4/1/68	0900	1210	0.030	0.037	0.024	0.029
4/1/68	1800	590	0.028	0.016	0.014	0.008
SUB-TOTAL		15,850		0.492		0.265
AVERAGE CONCENTRATION			0.031		0.017	
TOTAL		23,340		0.893		
AVERAGE CONCENTRATION			0.038		0.022	

TABLE 5-12

LEAD CONTENT OF RAINFALL -- NOVEMBER 1967 TO APRIL 1968

	Location		
	Freeway	Residential	Foothills
Total Rainfall Collected (inches)	7.80	11.40	11.20
Total Lead Collected (mg)	3.25	3.66	0.92
Average Total Lead Content (mg/l)	0.18	0.15	0.038
Average Total Lead Content Nov. 1 - Jan. 15 (mg/l)	0.28	0.18	0.053
Average Total Lead Content Jan. 15 - April 1 (mg/l)	0.14	0.13	0.031
Maximum Total Lead Concentration (mg/l)	1.00	0.50	0.13
Minimum Total Lead Concentration (mg/l)	0.027	0.006	0.011
Average Soluble Lead Content (mg/l)	0.056	0.042	0.022
Average Percent of Lead Which Was Soluble	31%	28.1%	58%

in rainfall are: Storm type and history, updraft velocity, rainfall intensity and duration, raindrop size, amount and characteristics of the lead pollutants present, number and type of potential nuclei available to compete with lead particles, and local topographic features. Therefore, it is difficult to obtain useful information by examining individual rainfall samples for lead content, but average values obtained from a large number of samples taken at various locations can be used to indicate general trends in the lead concentrations.

The results presented in Table 5-12 show easily detectable amounts of lead were contained in rainfall, especially in the samples collected near a major source of lead pollution. The average lead concentration in the rainfall collected at the freeway site was almost five times greater than the average concentration in the rainfall collected five miles away in the foothills. The average lead concentration found in the samples collected during the first part of the season (November 15 to January 15) was 40 to 50% higher at all three sites than the average concentrations found during the last half of the season. The exploratory samples taken randomly during the 1966-1967 season at the foothill and freeway sites also showed higher lead levels during the first part of the season.

During an extended rainfall period, the concentration of lead in rainfall should tend to decrease as the amount of atmospheric contamination is decreased. Since no lengthy storms occurred during the 1967-

1968 season, rainfall samples collected by others in earlier years were used to observe the changes in lead content during an extended rainfall period. Dr. Paul Kruger of Stanford University provided aliquots of samples collected during the storm of January 20-23, 1967. These samples were originally collected to determine the Ba^{140}, Sr^{90}, and Sr^{89} content of rainfall. The samples were collected at various locations along the California coast in 39 ft^2 collectors at six hour intervals. Aliquots of similar samples collected in January 1968 were also made available. Table 5-13 contains the results of the lead analysis on these six hour rain samples. The concentrations found during the 1967 storm are plotted as a function of time in Figure 5-14. With the exception of the rainfall collected at Bodega Bay, the lead concentrations tended to decrease as the storm continued, but small increases were noted in some samples. Increases in local traffic in areas such as Fort Bragg and Los Angeles could account for the increased lead content in some samples.

The minimum lead concentrations of 0.05 and 0.04 mg/l found at Bodega Bay and the light station at Piedras Blancas correspond well with the average level of 0.039 mg/l determined for rainfall collected at the foothills site in Palo Alto. Thus, lead levels of approximately 0.04 to 0.05 mg/l appear to be typical in the rainfall collected in relatively unpolluted areas along the California coast. In areas where

TABLE 5-13

LEAD IN RAINFALL SAMPLES
January 20 - 22, 1967

Site	Time (PST)	Precipitation (mm)	Lead Concentration (mg/1)
Arcata	1800	15.6	0.27
	2400	15.5	0.18
	0600	14.5	0.12
	1200	10.9	0.12
	1800	2.6	
	2400	0.5	
	0600	0.8	0.08
Fort Bragg	1800	13.7	0.22
	2400	11.3	0.24
	0600	19.3	0.15
	1200	8.1	0.21
Bodega Bay	1800	20.4	0.05
	2400	6.8	0.06
	0600	7.0	0.06
	1200	8.1	0.07
	1800	16.0	0.10
Pacific Grove	2400	2.0	
	0600	6.9	0.27
	1200	3.4	0.11
	1800	6.7	
	2400	37.9	0.13
Piedras Blancas	2400	3.0	
	0600	0.8	
	1200	0.4	0.17
	1800	3.4	0.04
	2400	22.7	0.11
Vandenburg Air Force Base	1800	0.1	
	2400	2.0	
	1200	16.5	0.19

TABLE 5-13, Continued

Site	Time (PST)	Precipitation (mm)	Lead Concentration (mg/1)
Goleta	2400	8.4	
	1200	19.3	0.09
	0600	4.6	0.06
Los Angeles	0600	7.6	0.50
	1200	44.5	0.13
	1800	8.5	0.27
	2400	4.3	0.24
La Jolla	1800	1.1	0.42
	2400	18.9	0.19
		January 15, 1968	
Bodega Bay		2.1	0.35
		4.0	0.58
		43.5	0.12
Pescadero		31.7	0.20
Pacific Grove		11.2	0.03
		2.0	0.24
Piedras Blancas		16.7	0.05
Vandenburg Air Force Base		2.2	0.38
Goleta		13.7	0.55
Los Angeles		4.2	0.65

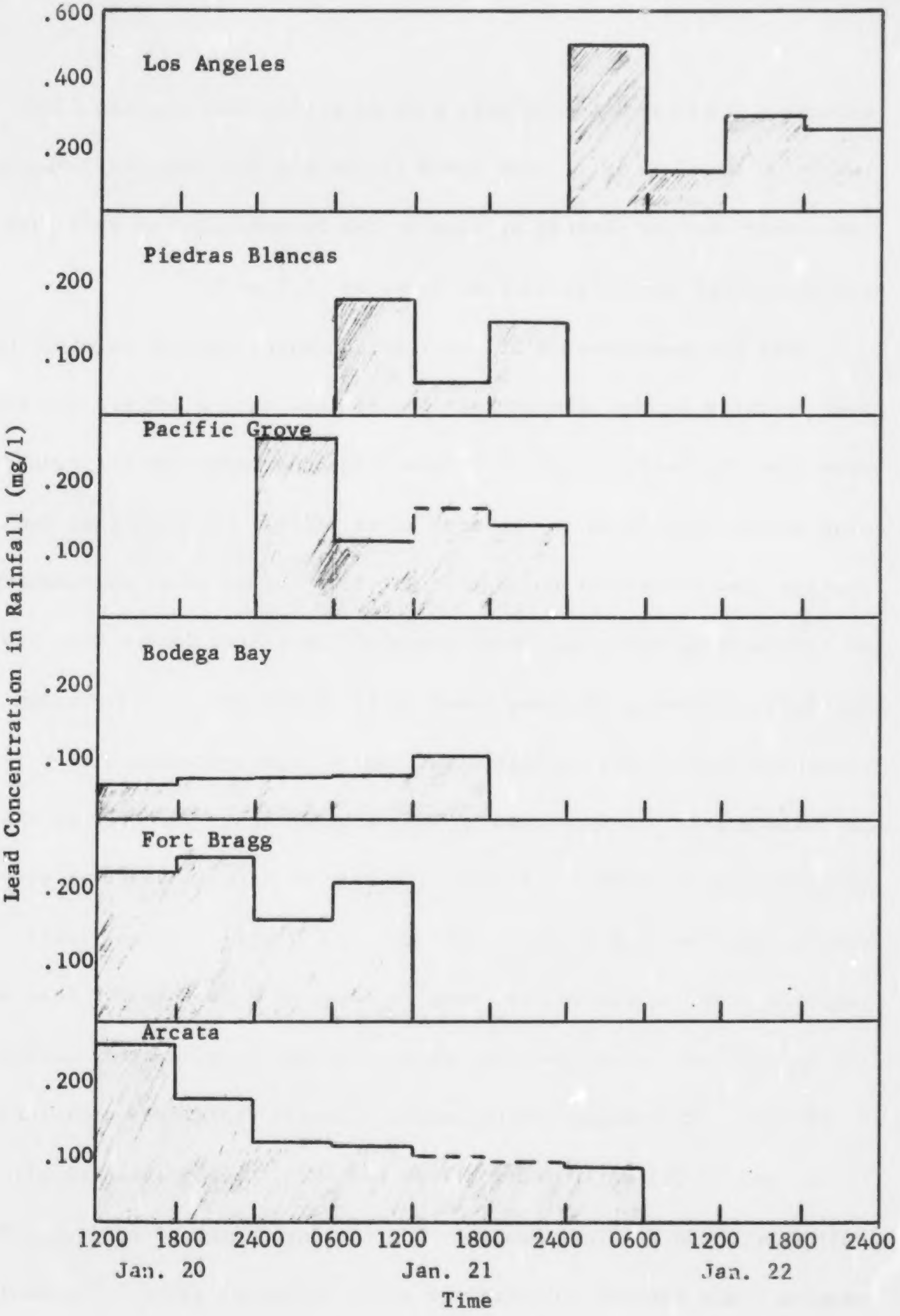


FIGURE 5-14
LEAD CONCENTRATION IN SIX HOUR RAINFALL SAMPLES
January 20-22, 1966

extensive lead pollution exists, such as Los Angeles and San Diego, levels up to 0.65 mg/l were found in the six hour samples. Samples taken over shorter periods of time at the freeway site in Palo Alto contained lead concentrations as great as 1.0 mg/l.

Very few measurements of the lead concentrations in rainfall have been reported in the literature. The limited data which are available show that the lead content of rainfall in other areas of the country also varies considerably. Lazarus et al. (1967) reported that the average lead concentration in precipitation collected at approximately 30 locations in urban and rural areas of the United States from September 1966 to January 1967 was found to be 0.034 mg/l. The average concentrations at the various sites ranged from approximately 0.115 mg/l in Philadelphia, to near zero in Northern Montana. The average rainfall concentration at Catalina Island, the only California sampling site, was reported to be between 0.016 and 0.035 mg/l. Cohen (1967) reported that, in Cincinnati, samples taken on a rooftop 200 feet above the ground level contained lead concentrations ranging from 0.0016 to 0.240 mg/l. Two samples taken beside a nearby expressway contained 0.030 and 0.208 mg/l. During 1964 and 1965, the Division of Air Pollution, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio examined rain samples collected at eight different sites. The analysis showed three out of 23 samples to contain in excess of 0.050 mg/l of lead (Ettinger, 1967).

4. Impaction Removal

A rainfall collector was placed under a tree at the freeway sampling site to catch the rainwater dripping from the leaves. These drippings contained a portion of the particulate matter removed by the falling rain and material which had collected on the leaf surfaces. The data are contained in Table 5-14. The total amount of water collected was equivalent to 4.85 inches of rainfall, only 62% of the amount collected nearby in an open area. This difference can be attributed to splash losses, retention by the foliage and evaporation. The lead and non-volatile solids contents of the drippings collected varied considerably from storm to storm and during a storm. Lead and solid concentrations were normally highest in the first drippings collected at the beginning of a storm and decreased in subsequent samples. The impaction data are summarized in Table 5-15. Average values of lead and non-volatile

TABLE 5-15

IMPACTION DATA - SUMMARY

Total Rainfall Collected	4.85 inches
Total Lead Collected	44.34 mg
Average Lead Content	3.94 mg/l
Average Soluble Lead Content (80% of Samples)	0.95 mg/l
Average Pb/NVS	0.75%
Soluble Pb/Total Pb	27.7%

TABLE 5-14

LEAD COLLECTED UNDER THE EIGHTEEN FOOT OLEANDER TREE

1 ft^2 Collector

Date	Time (PST)	Volume (ml)	Total Lead Conc. (mg/1)	Total Lead (mg)	Soluble Lead Conc. (mg/1)	Soluble Lead (mg)	Total Solids (g/1)	NVS (g/1)	Total NVS (grams)	Pb/NVS (%)
10/3/67		20	15.3	0.30						
10/9/67		40	10.5	0.40						
11/14/67		75	28.2	2.10	0.22	0.02	4.56	3.33	0.250	0.85
11/28/67		100	18.0	1.80	3.50	0.35	3.60	2.65	0.265	0.68
11/29/67		1000	5.00	5.00						
11/29/67		170	2.94	0.50						
11/30/67		190	3.12	0.60						
11/30/67		145	1.95	0.30						
12/3/67		90	4.10	0.36						
12/3/67		500	2.10	1.05						
12/4/67		190	3.10	0.60						
12/5/67		100	2.92	0.30						
12/12/67		45	24.60	1.10						
12/18/67		400	4.80	1.90	1.82	0.07	1.040	0.720	0.290	0.67
12/19/67		140	2.16	0.30	1.11	0.15	0.284	0.098	0.013	2.20
1/10/68		1100	4.40	4.80	1.10	1.21	0.702	0.438	0.480	1.00
1/14/68	1000	85	7.80	0.66	1.90	0.16				
1/14/68	1930	50	3.00	0.15	1.00	0.05				
1/15/68	0700	450	1.90	0.85	0.66	0.30	0.225	0.148	0.067	1.30
1/29/68	1200	600	3.25	1.96	1.20	0.66	0.675	0.375	0.222	0.88
1/30/68	1200	1200	0.81	0.98	0.39	0.47	0.204	0.116	0.140	0.70
1/30/68	1930	960	0.57	0.55	0.44	0.42	0.106	0.066	0.066	0.86

TABLE 5-14, Continued

Date	Time (PST)	Volume (ml)	Total Lead Conc. (mg/l)	Total Lead (mg)	Soluble Lead Conc. (mg/l)	Soluble Lead (mg)	Total Solids (g/l)	NVS (g/l)	Total NVS (grams)	Pb/NVS (%)
2/21/68		300	6.00	1.80	1.80	0.54	1.570	0.622	0.186	1.03
3/9/68	1200	800	6.25	5.00	1.86	1.49	2.100	1.100	0.880	0.57
3/12/68	1915	1000	3.00	3.00	1.00	1.00	2.000	0.560	0.560	0.53
3/13/68	0800	400	1.62	0.64	1.56	0.62	0.440	0.080	0.034	1.90
3/14/68	0800	460	1.36	0.62	0.73	0.34	0.610	0.198	0.091	0.69
3/16/68	1600	60	1.66	0.10	0.52	0.03				
4/1/68	0900	490	2.16	1.08	0.43	0.21	0.612	0.182	0.089	1.21
4/1/68	1800	410	2.04	0.84	0.57	0.23	0.446	0.152	0.062	1.34
TOTALS		11,270		44.44		8.33 (8,750 ml)			3.658	
AVERAGE CONCENTRATION			3.94 mg/l		0.95 mg/l					

solids content were determined by computing the total amount of each constituent collected during the year and dividing by the total volume of drippings collected. The means of the individual sample concentrations were not used because the sample sizes were not uniform. Soluble lead was not determined in some samples, so the average value reported is only for 80% of the drippings.

Norman (1963) reported that small particles ($< 44\mu$) are preferentially retained on leaf surfaces. Extremely small particles may be tightly bound to the surface by small hairs, surface pores, and tacky substances excreted by the leaves. Thus, the first water dripping from the leaf surfaces should remove the large particles rapidly, leaving the smaller particles to be removed at a slower rate by subsequent rainfall. If a constant evaporation loss and a logarithmic size distribution of lead compound particles on the leaf surfaces are assumed, the change in mass, dM, of lead on a leaf surface during a storm will be

$$\frac{dM}{dt} = cv - k\,Q\,\frac{M}{s}$$

where

c = the lead concentration of the falling rain

v = the rainfall volume per unit time

Q = the volume of drippings per unit time

s = the volume of water stored on the leaf surfaces before dripping begins ($\cong 0.21$ from field observations)

k = a constant < 1

Integrating and assuming $M = M_o$ at $t = 0$ as a boundary condition

$$M = \frac{cvs}{kQ} + M_o - \left(\frac{cvs}{kQ}\right) e^{-\frac{kQ}{s}t}$$

Using the data from the storm of January 29-30, 1968, and assuming $M_o = 4.0$ grams (twice the amount removed during t_1, the period of heaviest rainfall),

$M_1 = 2.04$ grams $\quad M_2 = 1.06$ grams $\quad M_3 = 0.51$ grams

$c_1 = 0.156$ mg/l $\quad c_2 = 0.027$ mg/l $\quad c_3 = 0.044$ mg/l

$t_1 = 3$ hours $\quad t_2 = 12$ hours $\quad t_3 = 12$ hours

$v_1 = 0.330$ l/hr $\quad v_2 = 0.160$ l/hr $\quad v_3 = 0.110$ l/hr

$Q_1 = 0.200$ l/hr $\quad Q_2 = 0.100$ l/hr $\quad Q_3 = 0.080$ l/hr

Solving for k in each case,

$k_1 = 0.220$ $\quad k_2 = 0.117$ $\quad k_3 = 0.152$

From these data

$$\bar{k} \cong 0.163 \pm 0.077$$

Using the data from the storm of March 12, 1968, and assuming $M_o = 6.0$ grams (twice the amount removed during t_1, the period of heaviest rainfall),

$M_1 = 3.0$ grams $\quad M_2 = 2.36$ grams $\quad M_3 = 1.74$ grams

$c_1 = 0.166$ mg/l $\quad c_2 = 0.150$ mg/l $\quad c_3 = 0.062$ mg/l

$t_1 = 5$ hours $\quad t_2 = 12$ hours $\quad t_3 = 24$ hours

$v_1 = 0.3$ l/hr $\quad v_2 = 0.04$ l/hr $\quad v_3 = 0.038$ l/hr

$Q_1 = 0.25$ l/hr $\quad Q_2 = 0.035$ l/hr $\quad Q_3 = 0.019$ l/hr

and solving for k,

$k_1 = 0.142 \quad k_2 = 0.125 \quad k_3 = 0.135$

From these data

$$\bar{k} \cong 0.133 \pm 0.008$$

The results indicate that k was a constant for a given situation. This suggests that, as a storm continues, more and more of the impacted material on the leaf surfaces is loosened and is available for removal by the drippings which flow across the leaves. If a larger value had been chosen for s, the corresponding value of k would have been larger; and if a smaller value had been chosen for s, k would have also been smaller. For example, if s had been set at 1.5 liters, $\bar{k}$ would have been approximately 1.0. However, a storage volume of 1.5 liters would require a 0.6 inch rainfall before dripping could begin. Field observations at the freeway site indicate that approximately 0.1 inches of rainfall (0.2 $1/ft^2$) was required before dripping began.

The lead to non-volatile solids ratio was determined for the drippings samples and the results show that the ratio is lower than that found in the air or dry fallout samples. The average value of 0.75% indicates that other inorganic material is more effectively impacted on the tree leaf surfaces or is more efficiently removed from the leaves by the rainfall. The average lead to non-volatile solids ratio in air was found to be approximately 0.04 (4%) near the freeway and the corresponding ratio in dry fallout was 0.011 (1.1%).

A large portion of the lead collected under the tree was soluble. An average of 27.7% (Table 5-15) of this lead passed the GF/4 filter pad, while only 6% (Table 5-5) of the lead collected in dry fallout passed. Thus, the soluble lead appears to be preferentially removed from the atmosphere by impaction on the leaf surfaces, or it is preferentially removed from the leaves by rainfall.

During the period from November 7, 1967 to April 1, 1968, when all significant rainfall in the Palo Alto area occurred, 44.3 milligrams of lead was collected in the one square foot collector located under the tree. During the same period, only 3.25 milligrams of lead/ft^2 was collected in the rainfall and 19.8 milligrams per square foot was collected in the dry fallout in a nearby open area. Impaction on the leaf surfaces and subsequent removal by rainfall accounted for a 92% increase in the amount of lead removed.

5. Summary of Field Data

Table 5-16 summarizes the field data taken in this study. This data shows that lead contamination is extensive in the Palo Alto area, especially near the heavily traveled Bayshore Freeway. Dry fallout and rainfall remove a large portion of the lead pollutants present, but as indicated by the average air concentrations at the various sites, a significant amount of lead remains airborne for long periods of time.

TABLE 5-16

FIELD DATA - SUMMARY

	Freeway	Residential	Foothills
Average Lead in Dry Fallout ($mg/ft^2 \cdot wk$)	0.92	0.24	0.153
Lead Removed ($mg/ft^2 \cdot yr$)	49.4	11.7	8.3
Average Lead in Rainfall mg/l	0.181	0.149	0.035
Lead Removed ($mg/ft^2 \cdot yr$)	3.25	3.66	0.92
Average Air Concentration ($\mu g/m^3$)	7.30	2.28	1.90
Pb/Total Solids in Air	0.042	0.018	0.016
Pb/NVS in Dry Fallout	0.0112	0.0102	0.0049

$$\frac{\text{Total Lead Removed Under Trees}}{\text{Total Lead Removed in Open Area}} = 1.88$$

Laboratory Studies

This portion of the work was undertaken to determine the rate of nucleation of water droplets to be expected on various lead compound aerosols and to relate the rates observed to the physical and chemical characteristics of the aerosol particles. Four compounds were chosen for this study: $PbCl_2$, $PbBr_2$, PbI_2, and $Pb(NO_3)_2$. These compounds exhibit wide differences in physical structure and chemical properties. The chemical and physical properties of these compounds, which may affect their nucleative properties as aerosols, are given in Table 5-17.

TABLE 5-17

CHEMICAL AND PHYSICAL PROPERTIES OF THE LEAD AEROSOL PARTICLES
(CRC Handbook of Chemistry and Physics, 46th Edition, 1962)

Compound	$PbBr_2$	$PbCl_2$	PbI_2	$Pb(NO_3)_2$
Molecular Weight	367.0	278.1	461.0	331.2
Density (g/cm^3)	6.63	5.85	6.16	4.52
Melting Point (°C)	373	501	402	470
Solubility (g/l) @ 20°C	8.44	9.9	0.44	376.0
Crystalline Form	Rhombic	Rhombic	Hexagonal	Cubical or Monoclinic

Other lead compounds, notably $PbCl_2 \cdot Br$, $2NH_4Cl \cdot PbCl \cdot Br$, and $NH_4 \cdot 2PbCl \cdot Br$, are more prevalent in automobile exhaust (Working Group on Lead Contamination, 1965), but their complex structures and uncertain (or unknown) chemical properties made them undesirable for use in this first study.

Lead chloride and lead bromide are slightly soluble compounds which have rhombic crystalline structures. They are present in small quantities in automobile exhaust, due to the reactions of the lead alkyl combustion products with chloride and bromide scavengers added to the gasoline. Lead bromide compounds are believed to be unstable in the atmosphere, undergoing photochemical decay and releasing gaseous bromine (Lininger, 1966). Lead iodide is a relatively insoluble compound with an hexagonal crystalline structure very similar to the structure of ice. It has been considered for use as a seeding agent for supercooled clouds for this reason. This compound does not appear to be present in automobile exhaust, but studies by Schaefer (1966) indicate that PbI_2 forms rapidly if a source of iodine is present in a system containing auto exhaust. $Pb(NO_3)_2$ is an extremely soluble compound with a cubical structure similar to $NaCl$. This compound may be present in small amounts in auto exhaust.

Aerosols of the four compounds were prepared by atomizing known solutions of each compound and drying the resulting droplets to obtain reproducible aerosols with the desired size distributions and number densities. These aerosols were introduced into the supersaturated environment inside the thermal gradient chamber where nucleation and droplet growth occurred. The larger droplets precipitated to the bottom surface where they were ultimately collected and analyzed for lead content. Any particles which did not act as condensation nuclei and droplets too small to be removed from the chamber by precipitation were wasted in the exhaust from the chamber.

The droplet growth in the chamber was observed and the resulting cloud of visible droplets was photographed through viewing ports in the chamber walls. It was determined from these observations that the droplet cloud began forming immediately after the aerosol injection began and, in most cases, filled the illuminated volume of the chamber within 60 seconds. The droplets were observed to fall through the illuminated volume at a speed of approximately 6 cm/min. The average droplet diameter, determined from random measurements of the photographed droplets, was approximately 40 microns, but the picture quality was such that more precise measurements could not be made. Even though high speed Kodak Royal X Pan Film (ASA 1250) and extended development techniques were used, one twenty-fifth of a second exposures were required to photograph the reflected light from the droplets. During this exposure period, the droplet movements (approximately 40 microns vertically and several microns horizontally) produced distorted images.

Four series of tests were run on the lead compound aerosols. The first and second series were conducted using the Coleman Atomizer which produced relatively large droplets, and the third and fourth series were conducted using the deVilbus nebulizer, which produced smaller droplets. The amount of lead collected from the bottom surface after each test was plotted against the temperature difference across the chamber. The temperature gradient, rather than the calculated degree of supersaturation in the chamber, was chosen as the independent variable. Once an aerosol was injected, the supersaturation in the chamber was no longer a function of the thermal gradient, but was controlled by the nuclei number density and the rate at which nucleation occurred. The thermal gradient, however, did control the rate at which heat and water vapor diffused from the surface, which, in turn, controlled the droplet growth.

At equilibrium, the quantity, Q, of water vapor diffusing from a surface can be approximated by

$$\frac{dQ}{dt} = \varkappa A \frac{dP}{dl}$$

where dP/dl is the vapor pressure gradient near the surface, A is the surface area and $\varkappa$ is a diffusion coefficient. The vapor pressure gradients in the boundary layers near the top and bottom surfaces are controlled by the temperature difference between the surfaces. The vapor pressure differences, ΔP, across these boundary layers are given in Table 5-18. Since the vapor pressure gradients increase in an almost linear manner as the temperature difference over the range of interest $(3^{o} - 10^{o})$ increases, the diffusion rate should also increase linearly. Therefore, an increase in the temperature difference between the chamber surfaces should produce a proportional increase in the amount of water vapor available for droplet growth and, hence, a proportional increase in the number of droplets growing to a size large enough for effective precipitation.

Least squares analyses were conducted on each set of data to estimate the relationship between lead collected and temperature differences according to the procedure outlined in Appendix A. The slope and intercept of the linear curve which best fit the data was determined, and the standard deviation of the data from this curve was calculated. The results of these analyses are summarized in Table 5-19. The standard deviations of the data from the lines of best fit were never larger than 5.0 micrograms. The largest deviations occurred when large amounts of lead aerosols (30 to 60 micrograms) were involved. Slight changes in air pressure could affect the air flow rate and the nuclei number density during the tests. These slight changes could account for much of the scatter in the data.

TABLE 5-18

TEMPERATURE AND VAPOR PRESSURE GRADIENTS IN THE CHAMBER

T_{Bottom} (°C)	T_{Top} (°C)	P_{Bottom} (mmHg)	P_{Top} (mmHg)	$\overline{P}$ (mmHg)	ΔP (mmHg)
17	20	14.53	17.53	16.03	1.50
16	20	13.63	17.53	16.58	1.95
15	20	12.79	17.53	15.16	2.37
14	20	11.99	17.53	14.76	2.77
13	20	11.23	17.53	14.38	3.15
12	20	10.52	17.53	14.02	3.51
11	20	9.84	17.53	13.68	3.85
10	20	9.21	17.53	13.36	4.17

TABLE 5-19

SUPERSATURATION CHAMBER RESULTS

Compound	Average Particle Size (μ)	Slope μg/°C	Intercept (μg)	Standard Deviation From Curve (μg)
$PbBr_2$	0.27	0.60	4.30	1.12
	0.50	3.05	7.40	2.71
	0.86	2.13	25.0	4.94
$PbCl_2$	0.27	0.56	3.30	0.67
	0.50	5.10	8.50	2.10
	0.93	3.04	29.0	5.0
PbI_2	0.27	0.17	1.50	0.9
	0.38	0.41	9.76	2.15
$Pb(NO_3)_2$	0.27	0.54	2.00	0.88
	0.47	0.94	7.00	2.9
	0.50	0.92	9.10	3.20
	1.00	1.00	28.9	2.78

1. Series I

Solutions containing approximately 1.0 mg/l of lead were atomized to produce particles calculated to have a mass median diameter of 0.50 microns. The actual mass median diameter results were found to be within 10% of the calculated value (see page 67). A less concentrated solution of PbI_2 was used because of its limited solubility. The mass median diameter was calculated to be 0.38 micron. The number density of the aerosols was controlled by the length of time that the solution was atomized. The most dense aerosol (3.1×10^4 nuclei/cm^3) was produced by atomizing for 50 seconds; the medium density aerosols (1.6×10^4 nuclei/cm^3) resulted from a 30 second spray and the least dense aerosol (1.0×10^4 nuclei/cm^3) was produced by atomizing for 15 seconds. The Series I data are given in Table 5-20.

Figure 5-15 is a plot of the Series I data with the least square linear curves added. The data seemed to fall near the linear curves regardless of the aerosol number density, until 100% of the available lead nuclei were removed. Then an increase in the temperature difference produced no change in the amount of lead collected.

The different slopes exhibited by the four compounds indicate that the chemical and physical properties did affect the rates at which nucleation occurred on the particles. A relatively flat slope indicates that the nucleation rate on the aerosol particles was rapid.

TABLE 5-20

SERIES I CHAMBER RESULTS
(0.50 μ)

$PbBr_2$		$PbCl_2$		PbI_2		$Pb(NO_3)_2$	
ΔT °C	Lead Collected (μg)	ΔT °C	Lead Collected (μg)	ΔT °C	Lead Collected (μg)	ΔT °C	Lead Collected (μg)
3.1×10^4 particles/cm^3							
3.0	18.0	3.0	24.5	3.5	10.4	3.5	11.1
3.0	14.0	3.5	26.2	5.0	11.2	4.0	14.0
3.5	17.8	5.0	32.0	6.0	11.4	5.5	12.0
6.0	27.2	5.0	33.0	7.0	12.0	5.5	15.9
7.5	30.0	5.5	35.0	8.0	13.8	7.0	12.5
8.5	32.5	5.5	35.5	9.5	12.5	7.0	18.0
10.0	33.5	5.5	36.2			8.0	13.3
		5.5	38.2			10.5	18.8
		6.0	37.5			11.0	18.6
		6.0	45.0				
		7.0	30.0				
		7.0	46.5				
		8.5	37.8				
		8.5	50.0				
		9.5	41.7				
		10.5	49.2				
1.6×10^4 particles/cm^3							
5.0	18.4	5.0	30.6	5.5	13.4	3.5	13.3
5.0	23.0	6.5	24.0	6.0	13.2	8.0	17.5
7.5	35.0	9.0	31.3	10.0	14.3		
8.0	32.5	9.5	31.5				
9.0	31.5	10.0	31.6				
		10.0	34.9				
		10.5	23.9				
		10.5	30.1				
0.98×10^4 particles/cm^3							
5.0	20.5	4.0	27.5			5.5	15.0
7.0	19.0	5.0	20.2			9.0	18.9
8.0	21.0	6.0	29.1				
9.0	23.9	7.5	19.7				
10.0	16.1	8.5	16.6				
		8.5	18.9				
		10.0	16.2				

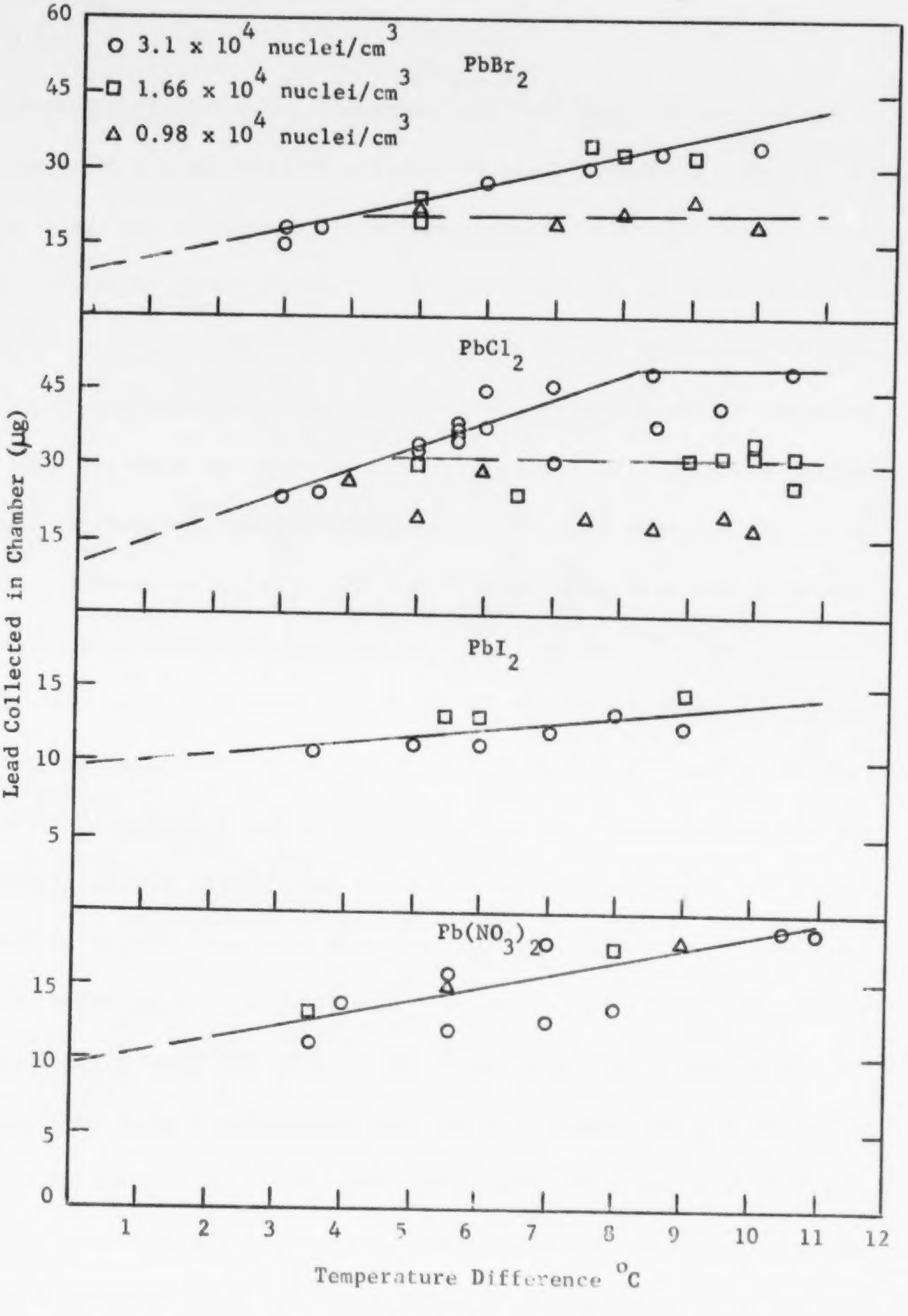


FIGURE 5-15
SERIES I DIFFUSION CHAMBER RESULTS
(0.50 μ diameter particles)

As the aerosol was injected into the chamber, the available moisture in the vicinity of the particles was quickly depleted by the rapid nucleation, and the degree of supersaturation was decreased. As the local supersaturation was lowered, many of the smaller newly formed droplets began to evaporate. Since the vapor pressure over a curved surface increases as the degree of curvature increases, the smallest droplets evaporated first. The larger ones, greater than the critical size determined by the minimum supersaturation reached, continued to grow, condensing the vapor made available by the evaporating droplets and that supplied by diffusion. When the growing droplets became large enough, they precipitated to the collection surface. Their removal from the system allowed the degree of supersaturation to again increase and the nucleating process was repeated with the same results--droplet growth and the removal of some nuclei. This dynamic condensation and evaporation cycle continued, but since the flow through time in the chamber was finite (100 seconds), some of the nuclei were wasted from the system before they produced droplets large enough to precipitate. An increase in the temperature gradient across the chamber had little effect on the number of nuclei collected. The rapid nucleation which decreased the local supersaturation was the controlling factor. However, when nucleation occurred more slowly, vapor diffusion from the chamber surfaces was better able to maintain supersaturation near the particles and the temperature gradient across the chamber had a larger effect. Thus, when nucleation occurred rapidly, the temperature gradient had little effect and a relatively flat slope resulted when the lead collected was plotted against ΔT. A steeper slope resulted if nucleation occurred more slowly.

When a less dense aerosol, i.e., fewer nuclei per unit volume, (represented by the symbols ○ and □ in Figure 5-15) was introduced into the chamber, nucleation occurred at the same rate, but the available vapor to particle ratio was somewhat greater. Hence, more droplets reached the critical size before the available moisture was depleted, and continued to grow. Therefore, even though the total number of nuclei available was smaller, the amount of lead collected when a less dense aerosol was injected, was comparable to the amount collected from a higher number density aerosol (slightly more in most cases). Temperature differences of less than 10° were large enough to effect 100% removal of the less dense $PbCl_2$ and $PbBr_2$ aerosols, as indicated by the horizontal curves in Figure 5-15.

PbI_2, the most insoluble compound, showed the smallest slope, which indicates the nucleation occurred rapidly on aerosol particles composed of $Pb(NO_3)_2$, the most soluble compound. $PbCl_2$ and $PbBr_2$ aerosols showed much steeper slopes, indicating that nucleation occurred more slowly on these particles, allowing the supersaturation to be better maintained by diffusion. The data indicate that, at temperature differences larger than 8°, the supersaturation in the chamber was maintained at all times when $PbCl_2$ particles were injected and all the available $PbCl_2$ nuclei were removed in the large droplets.

2. Series II

This series of tests was conducted to determine the effect of particle size on the nucleation rates of the compounds. More concentrated solutions of $PbBr_2$ (8.1 mg/1), $PbCl_2$ (9.3 mg/1) and $Pb(NO_3)_2$ (8.8 mg/1) were atomized with the Coleman Atomizer for 15 seconds to produce larger droplets. The number density was comparable to the number density of the least dense aerosol used in Series I. The mass median diameters were calculated to be 0.86 micron ($PbBr_2$), 0.93 micron ($PbCl_2$) and 1.00 microns $(PbNO_3)_2$. PbI_2 was not used in this series because of the insolubility of that compound.

The Series II data are contained in Table 5-21, and the amount of lead collected in each test is plotted as a function of the temperature difference in Figure 5-16. The amount of lead removed is plotted against the corresponding temperature difference between the top and bottom surfaces of the chamber. The slopes obtained in the first series of tests are shown as dashed lines. The slope obtained for the $Pb(NO_3)_2$ aerosol is slightly greater than the slope determined for the smaller sized particles. The slopes found for the larger $PbBr_2$ and $PbCl_2$

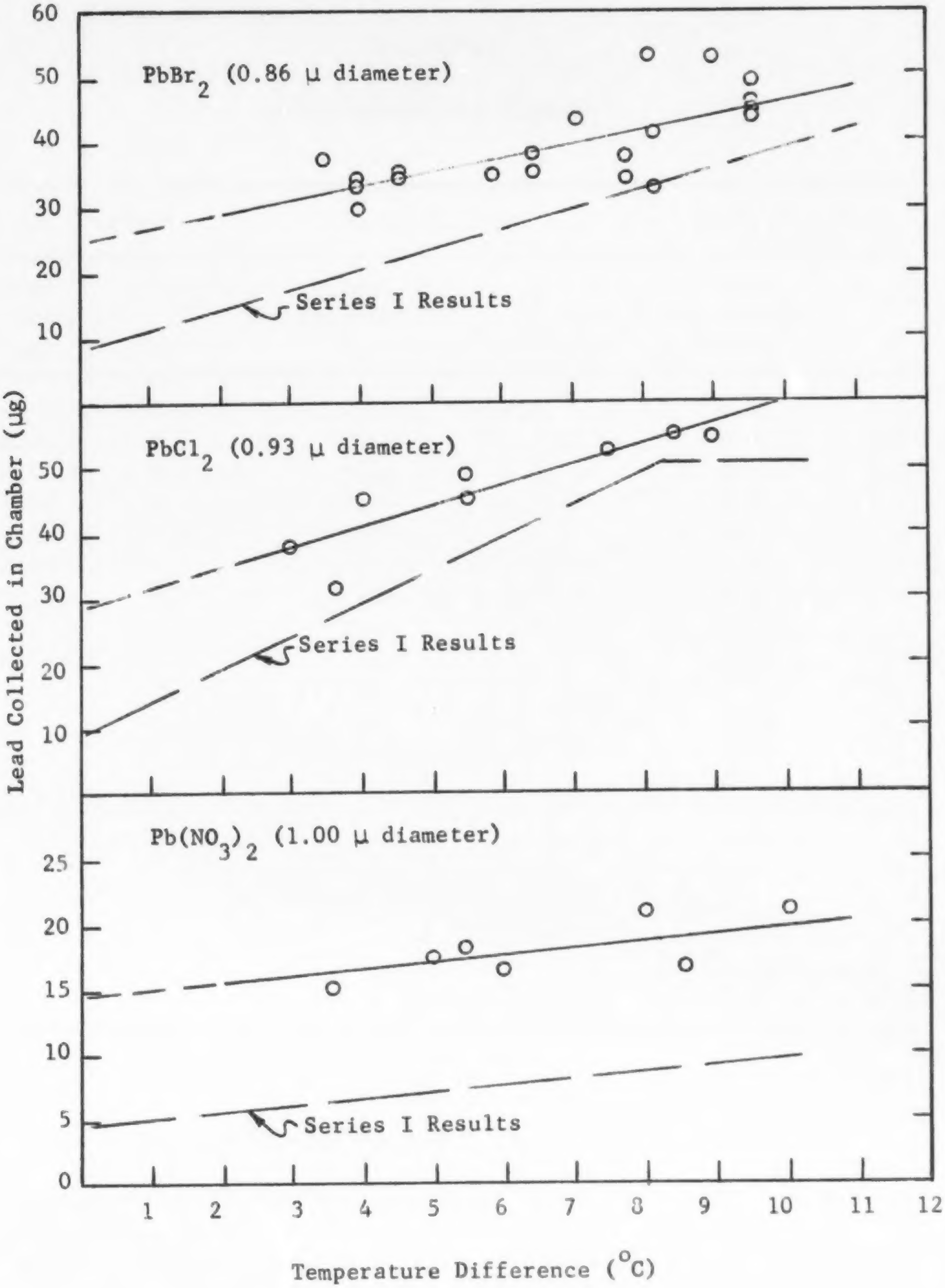


FIGURE 5-16
SERIES II DIFFUSION CHAMBER RESULTS
(1.0×10^4 nuclei/cm^3)

TABLE 5-21

SERIES II CHAMBER TESTS

$PbBr_2$ (0.86 μ)		$PbCl_2$ (0.93 μ)		$Pb(NO_3)_2$ (1.00 μ)	
ΔT °C	Lead Collected (μg)	ΔT °C	Lead Collected (μg)	ΔT °C	Lead Collected (μg)
3.5	38.8	3.0	38.0	3.5	30.0
4.0	30.0	3.5	31.0	5.0	36.0
4.0	33.0	4.0	46.5	5.5	37.0
4.0	33.8	5.5	46.5	6.0	32.5
4.5	34.0	5.5	49.0	8.0	41.0
4.5	35.1	7.5	52.5	8.5	32.5
6.0	35.8	8.5	55.5	10.0	41.0
6.5	35.7	9.0	54.0		
6.5	38.0				
7.0	43.0				
7.5	34.0				
7.5	37.5				
8.0	32.0				
8.0	41.0				
8.0	53.1				
9.0	52.0				
9.5	43.9				
9.5	44.9				
9.5	45.7				
9.5	48.1				

particles are much less than those obtained in the first series of tests. This decrease in slope, i.e., increase in nucleation rate for the larger $PbBr_2$ and $PbCl_2$ particles may have occurred because nucleation could begin simultaneously at several locations (active sites) on the larger surface. Several small caps of moisture may have formed first and merged to form a coating around the entire particle, as suggested by Fletcher (1961). The larger $Pb(NO_3)_2$ particles did not show an increased nucleation rate. Individual caps of moisture probably did not form on the more soluble (and more wettable) $Pb(NO_3)_2$ surface.

The $PbCl_2$ slope is reduced by 40% over that resulting from the 0.5 micron diameter particles and the $PbBr_2$ slope is decreased by 30%. The slight increase in the $Pb(NO_3)_2$ slope (10%) is within the statistical error of these measurements and may not be significant.

3. Series III

The third series of tests was conducted to observe the nucleation rate of small particles near the Aitken range. The deVilbus nebulizer, which is equipped with an impaction surface to remove large droplets from the airstream, was used to atomize the dilute solutions of the four compounds for 15 minutes, producing aerosols with mass median diameters of approximately 0.25 micron. The number density of these aerosols was comparable to the most dense aerosols used in Series I. The Series III data are given in Table 5-22.

The results, plotted in Figure 5-17, show that, with the very small nuclei, the rate of nucleation appeared to be independent of the aerosol compound. Within allowable error, the slopes determined were the same for $PbCl_2$, $Pb(NO_3)_2$ and $PbBr_2$. However, the slope obtained for the PbI_2 aerosol was somewhat lower.

TABLE 5-22

SERIES III CHAMBER TESTS
(0.27 μ)

$PbBr_2$		$PbCl_2$		PbI_2		$Pb(NO_3)_2$	
ΔT °C	Lead Collected (μg)	ΔT °C	Lead Collected (μg)	ΔT °C	Lead Collected (μg)	ΔT °C	Lead Collected (μg)
3.0	5.9	3.0	2.7	3.5	2.1	2.5	3.5
3.0	6.3	3.5	6.0	4.0	2.5	3.5	3.3
4.5	7.0	4.0	5.2	7.0	3.7	6.5	4.5
5.0	6.5	5.5	5.5	8.0	1.6	7.0	6.5
5.0	7.3	7.0	3.7	8.5	3.0	8.0	6.5
5.0	7.6	7.0	8.0	9.0	4.0	8.0	7.7
6.5	8.4	7.5	6.7			10.0	6.5
8.0	10.5	7.5	7.2				
9.0	8.4	7.5	8.4				
9.0	9.4	7.5	8.9				
9.0	12.0	8.0	7.2				
10.0	8.5	8.5	7.4				
		8.5	9.2				

4. Series IV

This series was attempted to establish a basis for comparison between the Series I and Series III results. Since the aerosols used in these tests were produced by two different nebulizers, the Series IV tests were conducted to determine whether or not aerosols with approximately the same mass median diameter (but generated by different nebulizers) would react in the same manner in the chamber. The more concentrated solutions of the three compounds were atomized with the

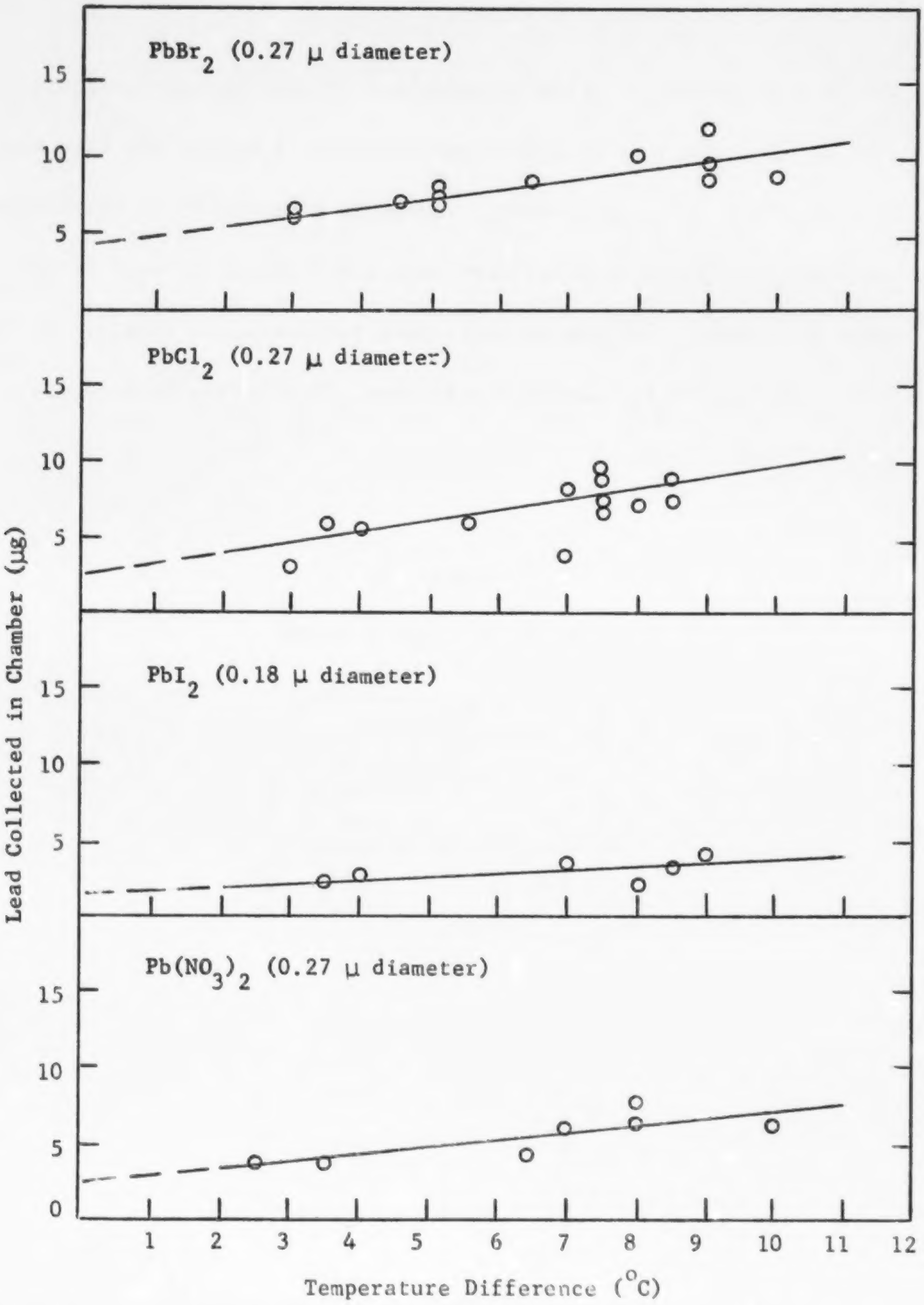


FIGURE 5-17
SERIES III DIFFUSION CHAMBER RESULTS
(4.5×10^4 nuclei/cm^3)

deVilbus nebulizer to produce aerosols with mass median diameters similar to those used in the Series I tests. However, the saturated solutions of $PbCl_2$ and $PbBr_2$ tended to crystallize in the deVilbus nebulizer, clogging the capillary tube and forming deposits on the impaction plate. Uniform aerosols were impossible to obtain. Therefore, only $Pb(NO_3)_2$ aerosols were used. The Series IV data are given in Table 5-23.

TABLE 5-23

SERIES IV CHAMBER TESTS
(0.47 μ)

$Pb(NO_3)_2$	
ΔT °C	Lead Collected (μg)
3.0	9.0
4.0	10.4
4.5	12.0
5.5	12.9
6.0	12.2
7.0	20.0
7.0	14.8
8.0	11.3
8.5	14.9
9.5	13.1
10.0	16.2

Figure 5-18 is a plot of the lead collected as a function of the temperature difference. There was considerable scatter in the data, but the least squares analysis was performed using all the points.

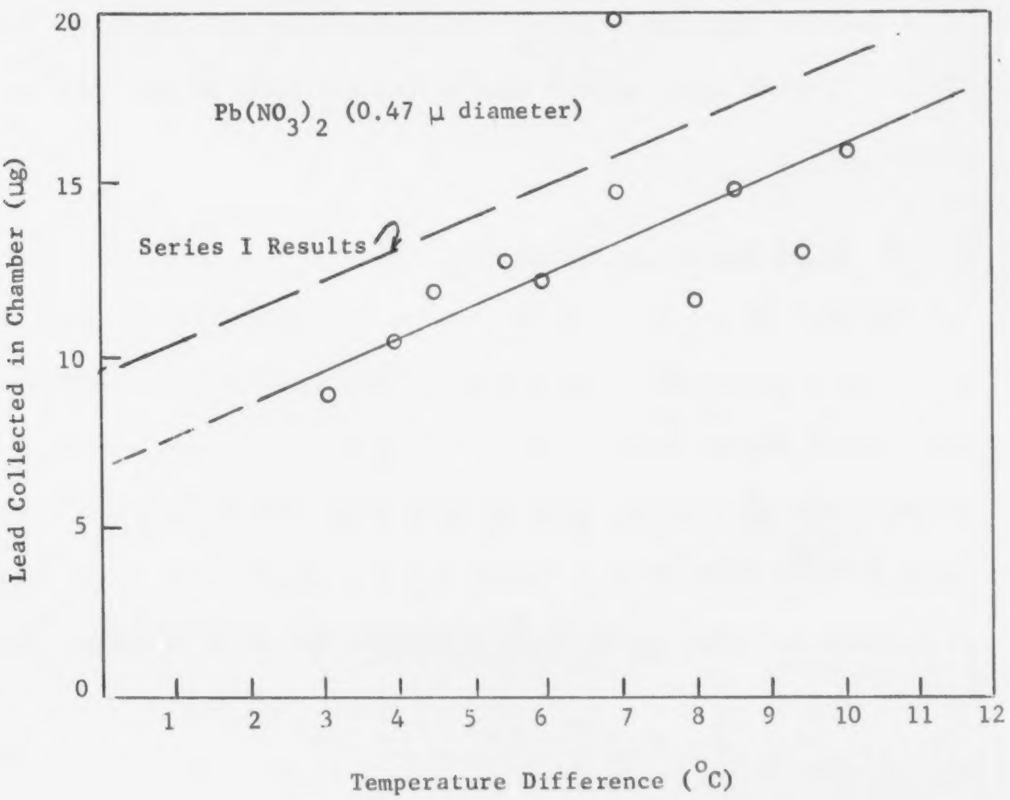


FIGURE 5-18
SERIES IV DIFFUSION CHAMBER RESULTS
(4.5×10^4 nuclei/cm^3)

The slope obtained was very near that found for the $Pb(NO_3)_2$ aerosol in Series I. These results suggest that the aerosols produced by the two nebulizers reacted in a similar manner in the chamber. Therefore, the results obtained from the Series III tests may be compared to the Series I and II results. The smaller slopes obtained in the Series III tests indicate that the extremely small particles acted as nuclei for droplet formation more rapidly than larger particles of the same composition.

5. Cloud Density Determinations

Random droplet size measurements and droplet counts were made on the Series I photographs when possible. Poor quality photographs and high droplet number densities often made such measurements impossible. The available data are included in Table 5-24. The ratio given is the ratio of the total lead collected from the bottom surface to the number of droplets contained in the photographed volume of the chamber. Several typical photographs showing the droplet density and droplet motion are reproduced in Figure 5-19.

Calculations to determine the lead concentration in each droplet can be made using these data and the following information:

Chamber Volume = 2380 cm^3

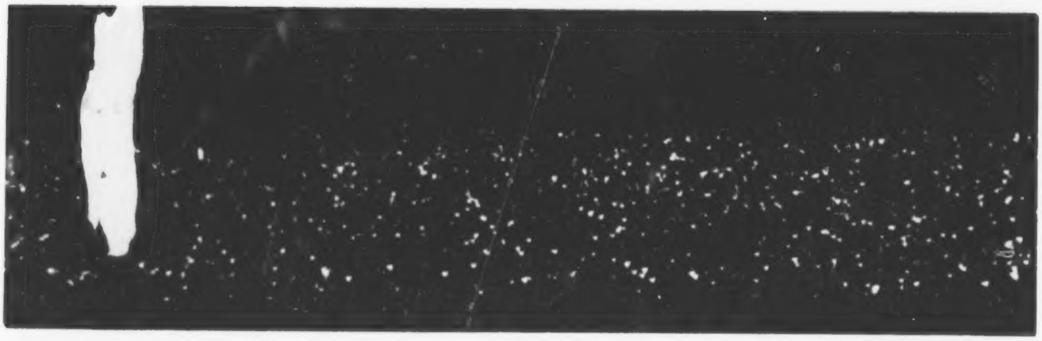
Picture Volume = $\pi R^2(L) = \pi(.15)^2(4.28 \text{ cm}) = 0.290 \text{ cm}^3$

Aerosol Mean Size = $0.50\ \mu$ diameter

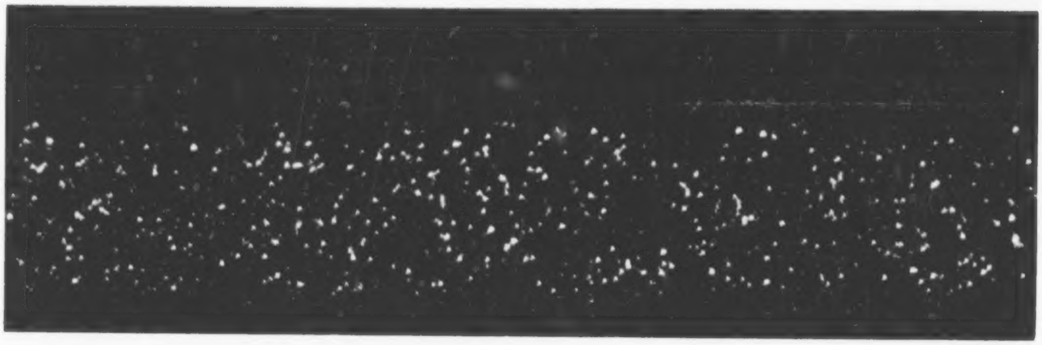
TABLE 5-24

DROPLET CONCENTRATION IN PHOTOGRAPHED VOLUME
(Series I Tests)

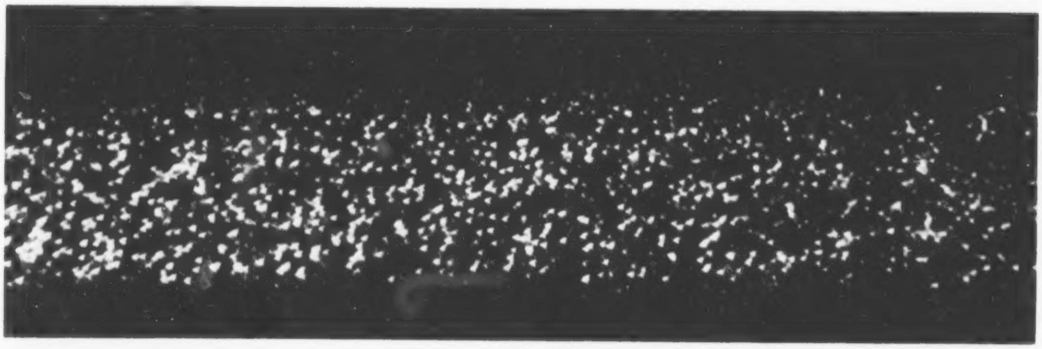
$PbBr_2$		$PbCl_2$		PbI_2		$Pb(NO_3)_2$	
Lead Collected (μg)	Ratio	Lead Collected (μg)	Ratio	Lead Collected (μg)	Ratio	Lead Collected (μg)	Ratio
10.8	0.0157	17.5	0.0725	13.8	0.0099	18.0	0.0234
20.1	0.0745	17.5	0.0835			14.9	0.0192
29.9	0.0703	19.4	0.0342			15.0	0.0396
27.2	0.0806	26.2	0.0377			18.6	0.0202
26.0	0.0162	35.5	0.0307			5.8	0.0137
17.8	0.0405	38.2	0.0179			26.6	0.0560
14.0	0.0583	33.0	0.0346			8.1	0.0360
___	___	32.0	0.0346			14.0	0.0185
AVERAGE =	0.0509		0.0432				0.0283



$Pb(NO_3)_2$ - 18.0 μg - 930 droplets/cm^3



$PbCl_2$ - 32.0 μg - 3100 droplets/cm^3



$Pb Br_2$ - 26.0 μg - 5500 droplets/cm^3

1 mm

Figure 5-19

Droplet Photographs

Aerosol Mean Volume = $4/3\ \pi R^3 = 6.5 \times 10^{-14}\ \text{cm}^3$

Mean Droplet Size = 40 μ diameter

Mean Droplet Volume = $4/3\ \pi r^3 = 3.36 \times 10^{-8}\ \text{cm}^3$

Droplet Fall Velocity (observed) = 6 cm/min

Average distance to collection surface = 1.5 cm

Assuming that the cloud density remains constant during the aerosol injection period (five minutes) and dissipates quickly after the injection ends, the total number of droplets, N, formed in the chamber will be

$$N = N' \frac{2380\ \text{cm}^3}{.290\ \text{cm}^3} \times \frac{6\ \text{cm/min}}{1.5\ \text{cm}} \times 5\ \text{mins}$$

$$= 1.66 \times 10^5\ N'$$

where N' is the number of droplets in the photographed volume. Therefore, the average lead concentration, $\bar{c}$, in the droplets formed will be

$$\bar{c} = \frac{\text{Ratio from Photograph}}{1.66 \times 10^5}\ (\mu\text{g/droplet})$$

The average amount of lead, $\bar{c}'$, in each nuclei can be determined by

$$\bar{c}' = 6.5 \times 10^{-14} \rho f \text{ grams}$$

where

6.5×10^{-14} = volume of 0.5 µ particles

ρ = particle density

f = fraction of mass of particle that is lead

TABLE 5-25

OBSERVED AVERAGE AMOUNT OF LEAD IN DROPLETS AND CALCULATED AMOUNT OF LEAD IN AEROSOL PARTICLES (SERIES I TESTS)

Aerosol Compound	$PbBr_2$	$PbCl_2$	PbI_2*	$Pb(NO_3)_2$
Average Lead to Droplet Ratio	0.0509	0.0432	0.0099	0.0283
ρ (g/cm^3)	6.66	5.85	6.16	4.53
f	0.565	0.754	0.45	0.625
c' (µg/particle)	3.06×10^{-7}	2.60×10^{-7}	0.6×10^{-7}	1.7×10^{-7}
$\bar{c}'$ (µg/particle)	2.46×10^{-7}	2.87×10^{-7}	0.8×10^{-7}	1.84×10^{-7}

*For PbI_2 (0.38 µ particles), $\bar{c}' = 2.88 \times 10^{-14} \rho f$

The good agreement between $\bar{c}$ and $\bar{c}'$ indicate that a one-to-one relationship existed between the nuclei removed and the droplets formed. Therefore, it can be assumed that the lead particles were removed only after acting as nuclei for droplet formation.

The amount of water, v, condensed to remove each microgram of lead can be determined by

$$v = 3.36 \times 10^{-8}/\bar{c} \text{ cc}/\mu\text{g}$$

where 3.36×10^{-8} = volume of a 40 μ droplet.

TABLE 5-26

AMOUNT OF WATER CONDENSED TO REMOVE EACH μg OF LEAD (SERIES I TESTS)

Aerosol Compound	$PbBr_2$	$PbCl_2$	PbI_2	$Pb(NO_3)_2$
$\bar{c}$ (g/particle)	3.06×10^{-7}	2.60×10^{-7}	0.6×10^{-7}	1.7×10^{-7}
v (cc/μg)	0.110	0.129	0.560	0.197

CHAPTER 6

DISCUSSION

The data presented in the preceeding chapter were collected to observe the bulk lead contaminants in the atmosphere and specific lead aerosol particles under controlled laboratory conditions. The data deal with different circumstances and will therefore be discussed separately, but the results of both phases of this work are complimentary and conclusions will be drawn based on all the data.

Field Study

In general, the data obtained in the field study portion of this program show that lead pollution is extensive in the Palo Alto area. Lead was present in the air, dry fallout and rainfall at all the sampling sites. The high speed, high density Bayshore Freeway traffic appears to be a major source of lead pollutants, with higher concentrations of lead in all samples collected near the freeway. The degree of contamination decreases rapidly with distance from the freeway, but lead was easily detected at the foothills site five miles away. A portion of the contamination observed away from the freeway is probably due to local traffic in Palo Alto and surrounding communities, but this local contribution should be small compared to that from the freeway. At freeway speeds 70% to 80% of the lead in gasoline is exhausted, while only 30 to 40% is exhausted at normal city driving speeds. This factor, plus the smaller number of automobiles used near the residential and foothills sampling sites, account for the minor contribution ascribed to local traffic.

The air samples obtained show that the concentration of lead pollutants in the atmosphere is highly variable, especially near a heavily traveled roadway. Lead concentrations ranging from 0.6 to 19 $\mu g/m^3$ were observed near the Bayshore Freeway and concentrations of 1.0 to 5.5 $\mu g/m^3$ were found in areas removed from high density traffic. The highest levels of airborne lead pollution were found near the freeway during the morning rush period. During the early morning hours when no winds were observed, the airborne lead concentrations found at the freeway corresponded well with the traffic flow past the sampling point. The expression which best described the data was found to be

$$L = 0.6 + 0.09\ F \qquad (5\text{-}1)$$

where

L = lead concentration ($\mu g/m^3$)

F = traffic flow (vehicles/minute)

This linear relationship indicates that an expression may be developed to predict the maximum lead pollution levels that will occur at a major freeway.

If the assumption is made that a well defined zone of turbulence is created by the moving traffic and that instantaneous and complete mixing occurs throughout this zone, the changes in lead concentration, L, in the zone can be represented by

$$\frac{dL}{dt} = \frac{I}{v} + \frac{Q}{v} K - \frac{Q}{v} L \qquad (6\text{-}1)$$

where

I = rate of lead input to the turbulent zone ($\mu g/min$)

v = volume of the turbulent zone (m^3)

Q = outflow of polluted air from the turbulent zone (m^3/min)

K = average lead concentration in the atmosphere outside the turbulent zone ($\mu g/m^3$)

t = time (min)

Without winds, the outflow, Q, from the turbulent zone is controlled by the convective currents rising from the roadway and the mixing which occurs at the boundary of the turbulent zone. If short time intervals are considered (< 15 minutes), this outflow will be relatively constant. Since the traffic flow does not change radically during short time intervals, the lead input to the turbulent zone may also be held constant.

Integration of (6-1), assuming $L = L_o$ at $t = 0$ as a boundary condition, yields

$$L = \left(\frac{I}{Q} + K\right)\left(1 - e^{-Qt/v}\right) + L_o e^{-Qt/v} \qquad (6\text{-}2)$$

Thus, if the traffic flow is relatively constant and calm conditions prevail, the concentration of airborne lead pollutants at the freeway will tend toward $(I/Q + K)$ in micrograms per cubic meter as t increases.

Since the average vehicle exhausts approximately 65 μg of lead per meter of travel (page 10), the input to each one meter section of the turbulent zone, I_1, can be estimated by

$$I_1 = 65(F)\ \mu g/\text{min}$$

where F = traffic flow (vehicles per minute). The airborne lead concentration at the freeway site can be estimated from the expression

$$\bar{L} = 0.6 + 0.09F \qquad (5\text{-}1)$$

and a value for Q_1 (outflow from each one meter section of the turbulent zone) can be determined.

$$Q_1 = \frac{I_1}{\bar{L} - K} = \frac{65(F)}{0.6 + 0.09(F) - K} \qquad (6\text{-}3)$$

Since K, the atmospheric lead concentration outside the turbulent zone, is small in the morning hours, the value of Q_1 can be approximated by

$$Q_1 = \frac{65(F)}{0.09(F)} \approx 720 \text{ m}^3/\text{min}$$

This large value for Q_1 during periods of calm suggests that the size of the turbulent zone will be relatively unimportant in equation (6-2). The value $e^{-Qt/v}$ will grow small rapidly as t increases and L will rapidly approach $\bar{L}$. Any traveller using a high speed roadway with a traffic flow sufficient to maintain a well mixed zone of turbulence will be subjected to maximum atmospheric lead concentrations approaching the value $65\ F/Q\ \mu g/m^3$. The value of Q for a given roadway can be determined by obtaining several air samples and traffic counts and solving equation (6-3).

The maximum concentrations will occur during periods of low wind and high atmospheric stability. Winds and unstable conditions will increase the atmospheric turbulence and the ventilation (Q) of the turbulent zone. The effects of this increased ventilation are evident in Figures 5-1 through 5-6, which show lower values of L in the afternoons, even though the traffic flow is greater during the evening rush period. No correlation between the afternoon values of L and the corresponding wind velocities was found. Data on wind variability and direction, temperature lapse rates and uplift velocities would be necessary to establish a good correlation between observed lead concentration, traffic flow, and atmospheric conditions.

The airborne lead concentrations decrease rapidly with distance from the freeway. This decrease is caused by atmospheric dilution and the removal of the lead pollutants from the atmosphere. Most investigators report that lead pollutants from automobiles are exhausted predominantly in the form of small inorganic particles which should remain airborne for long periods of time. However, the dry fallout data obtained in this study indicate that much of the lead exhausted by automobiles is removed by sedimentation. Approximately 60% of the lead produced by the freeway traffic can be accounted for in the dry fallout collected within five miles of the source. This agrees with estimates made by Hirschler et al. (1957). They reported that, in 1954, approximately 4.68×10^6 gallons of gasoline were consumed daily in the Los Angeles Basin, and the average lead content of this fuel was

2.2 g/gal. Thus, 10.3 x 10^6 grams of lead pollutants were exhausted into the basin each day. The volume of the Los Angeles Basin was estimated to be 4.2 x 10^{13} ft^3 when a 2000 foot inversion layer existed. Thus, the average lead content of the atmosphere should have reached approximately 9.2 $\mu g/m^3$ if no dilution occurred during a 24 hour period. However, air samples taken under these conditions indicated that the average air concentrations were lower than the calculated levels. The average values over the entire basin were approximately 4 to 5 ug/m^3. Hirschler et al. (1957) reported that these calculations suggest that a large proportion of the lead pollutants were removed from the atmosphere within the basin.

The fallout data obtained in this study also indicate that a linear relationship may exist between the lead and dust in dry fallout. The curves shown in Figures 5-10 and 5-11 suggest that the lead particles (presumably submicronic-sized) are removed in the same manner as the larger dust particles. An increase in dustfall results in a proportional increase in lead removal and a decrease in dustfall is accompanied by a proportional decrease in lead removal. These linear relationships between lead and dustfall and the rapid removal of lead pollutants by dry sedimentation suggest that the submicronic lead compound particles initially exhausted may become attached to the larger particles present in the atmosphere, which are significantly affected by gravity.

A process by which the submicronic lead aerosol particles may become attached to larger inorganic particles could occur in the automobile exhaust plume. Submicronic particles are very mobile and easily avoid collisions with other particles and surfaces making coagulation and impaction ineffective. However, when the hot exhaust gases from an automobile begin to cool rapidly in the exhaust system and the atmosphere, the gas stream containing the lead pollutants will become supersaturated with water vapor. This produces an environment in which water droplets can grow, using lead particles and other particulate matter as nuclei. The water droplets will be short-lived, evaporating as dispersion and mixing reduce the relative humidity around them. However, during the lifetime of the droplets, they will be rapidly mixed with other droplets and larger dust and combustion product particles entrained by the turbulence of the moving traffic, increasing the opportunity for collisions and impaction to occur.

If a droplet containing a lead compound nuclei impacts on a larger particle, the moisture will ultimately evaporate and the lead nucleus will remain loosely attached. Any sampling procedure employing impaction or centrifugation techniques may break many of these bonds and separate the lead aerosol particles from the larger particles. The number of small particles thus dislodged will depend upon the sampling technique used, perhaps accounting for the wide variety of size distributions of atmospheric lead reported in the literature. Even though many of the lead particles will behave as the large particles to which they are attached, the size distribution tests, which dislodge impacted lead particles from the larger particles, will indicate that the lead pollutants should behave as submicronic particles. Therefore, a much larger amount of lead is removed from the atmosphere by sedimentation than would be expected from the aerosol size distribution results.

The extensive variations observed in the amount of lead collected in the weekly dry fallout samples (Figure 5-12) were probably caused by variations in atmospheric conditions. The traffic flow did not change extensively from week to week, so the lead input was relatively constant. High relative humidity and low wind speeds should increase the amount of lead pollutants removed in dry fallout if the nucleation hypothesis previously discussed is correct. The droplets formed in the supersaturated exhaust stream will retain moisture longer if the relative humidity is high, and the larger particles upon which the droplets may impact will be removed from the atmosphere more effectively if the wind speeds are low. Likewise, low relative humidity and high wind speeds should have the opposite effect. Other factors, including temperature, radiation energy, uplift velocities, etc., may also contribute, but their effects should be small, especially during the summer and fall when atmospheric turbulence is low. A ratio of the average relative humidity to wind was calculated each week. The average relative humidity was determined from the daily readings at 0700 and 1600 PST taken at the San Francisco International Airport U. S. Weather Bureau Station. The total miles of wind movement each week were obtained from the U. S. Weather Bureau Station at Newark, four miles from Palo Alto. Figure 6-1 is a plot of this ratio as a function of time, and a corresponding plot of the weekly fallout data collected at the freeway. A fair correlation was found between the humidity-wind ratio and the amount of lead removed during the summer and early fall. From May 13 to November 13, 1967, and April 3 to May 30, 1968, 34 samples were collected, and 26 of these showed increased levels of lead removal when the relative humidity-wind ratio increased, or decreased levels of lead removal when the ratio decreased. The correlation coefficient was found to be 0.68. However, during the rainy season, the correlation was not good. Atmospheric turbulence was greater during this period, and the relative humidity-wind ratio decreased in importance. A negative correlation coefficient of - 0.47 was found for the samples collected from November 13, 1967 to April 3, 1968, indicating that high winds and low humidity tended to increase the amount of lead removed by sedimentation during the rainy season. The correlation coefficients were calculated according to the rank difference method outlined in the CRC Standard Mathematical Tables published by the Chemical Rubber Publishing Company, Cleveland, Ohio.

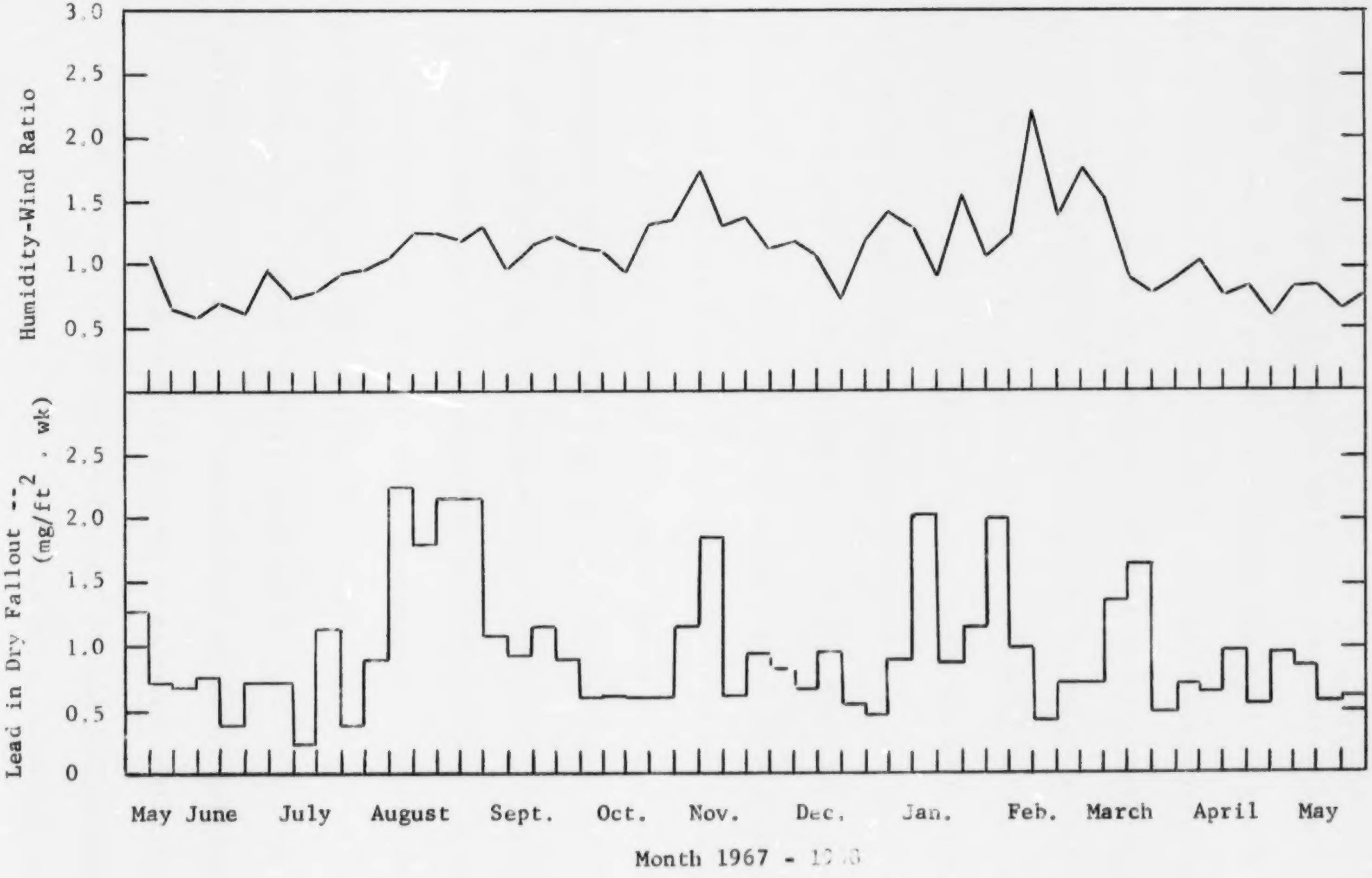


FIGURE 6-1

LEAD IN WEEKLY DRY FALLOUT SAMPLES AT THE FREEWAY AND WEEKLY RELATIVE HUMIDITY-WIND RATIOS

The increase in the percentage of soluble lead in the dry fallout collected at the sites removed from the freeway shows that the insoluble particles tended to be removed more rapidly. Several factors could account for the unequal removal rates:

1. The more insoluble lead particles may be larger initially and more likely to act as nuclei for droplet formation.
2. The more insoluble lead particles may be more attractive chemically as nuclei for droplet formation.
3. All the lead particles used as condensation nuclei may produce droplets of essentially the same size, but the droplets with soluble nuclei may be able to retain their moisture for a longer period of time. This would allow the more soluble nuclei to be available for impaction as droplets at greater heights and distances from the freeway.

The third explanation seems to be the most plausible. The vapor pressure over a solution droplet will be less than that over a pure water droplet (see Raoult's Law, page 41) so that droplets with soluble nuclei will evaporate more slowly. Studies by Dessins (1949) showed that droplets with NaCl nuclei may exist for long periods at relative humidities as low as 40%. Since an average of 6% of the lead collected as dry fallout at the freeway site was soluble, it may be assumed that approximately 6% of the lead aerosol produced by traffic was in a soluble form. (Robinson (1963) estimated this value to be near 9%.) As the polluted air was carried upward and away from the freeway, the more soluble nuclei continued to impact on larger atmospheric particles which could be removed by gravity. The insoluble particles lost moisture more rapidly and impacted less efficiently as they moved from the freeway, so a smaller proportion of these particles entered the fallout at the collection sites away from the traffic. This indicates that the soluble lead particles should be removed more completely than the insoluble particles.

The attachment of small lead particles to larger particles was also indicated by the rainfall data presented in the previous chapter. The rainfall collected near the freeway contained a large amount of lead, an average of five times the amount contained in the rainfall collected at the foothills site only five miles from the traffic. Higher concentrations were also noted in six hour samples collected along the California coast in heavily populated areas, including Los Angeles, La Jolla, and Fort Bragg. This increase in lead in rainfall was probably due to raindrop scavaging from the polluted air near the freeway. However, raindrop scavaging is inefficient for submicronic size particles, so the lead particulate matter removed by rainfall probably was associated with larger particles. The air samples taken during periods of rainfall showed that the lead content of the atmosphere was reduced somewhat by rainfall, but that substantial pollution remained.

The rainfall collected during the first half of the rainfall season (November 1-January 15) contained higher lead concentrations than the rainfall collected during the latter half of the season (January 15 - April 1). The higher lead concentrations in rainfall corresponded well with a study conducted during 1961-1962 in Los Angeles by the Working Group on Lead Contamination (1965), which indicated that the amount of lead pollution present in the atmosphere over that city was substantially greater during November, December and January than during the late winter and early spring. The reasons for the increased pollution levels during the fall are not fully understood, but the stable atmospheric conditions during this season probably play an important role.

The liquid or solid water contained in a cloud at a particlar time is rarely sufficient to provide more than a trace of precipitation (Fleagle, 1963). Therefore, in order to produce a significant amount of rainfall, an updraft must provide a continuous and plentiful supply of moisture to the cloud. This updraft will also provide an abundant supply of nuclei for raindrop formation. Even though certain local areas near the surface may be subjected to higher concentrations of particular pollutants (such as the freeway area in Palo Alto), it can be assumed that the turbulence and mixing which accompanies a convective cell will result in a relatively uniform supply of nuclei to all parts of a cloud. Then the amount of material being removed by rainout (nucleation in the cloud) at a given time during a storm will be relatively uniform over a large area. However, amounts of material being removed by washout (raindrop scavaging below cloud level) will be dependent upon the amount of material available near the surface, which is highly variable. Thus, the concentration, C, of lead in rainfall at a particular time can be divided into two parts:

$$C = C_R + C_W$$

where C_R is the amount resulting from rainout and is relatively constant over a given area, and C_W is the amount resulting from washout and is dependent upon the concentration of lead pollutants near the surface.

The minimum concentrations of lead present in rainfall were found in samples collected at the foothills site in Palo Alto, and in relatively unpolluted areas along the California coast. The minimum rainfall concentrations found in these areas was approximately 0.04 mg/l. Since nearly all populated areas of California receive some surface lead pollution, a portion of the 0.04 mg/l resulted from raindrop scavaging and the remainder entered rainfall in the growing cloud. Rainfall samples taken in or just below the clouds from aircraft or balloons would be necessary to accurately determine the exact portion of the lead removal resulting from rainout. However, in the absence of such information, it was assumed that 50% of the lead in the rainfall collected in relatively unpolluted areas resulted from rainout. Then,

$$\overline{C}_R = (.5)(0.04) = 0.02 \text{ mg/l}$$

Nucleation and subsequent growth by condensation in a cloud produces droplets of 20 to 60 microns radius, which undergo further growth by accretion (Fleagle, 1963). Thus, a condensation nuclei is needed to produce a volume of water, v, which can be determined by

$$v = 4/3 \, \pi \, r^3 \text{ cm}^3$$

For r = 20 microns

$$v = 4/3 \, \pi \, (2 \times 10^{-3})^3 = 3.30 \times 10^{-8} \text{ cm}^3$$

According to Robinson (1964), the mass median equivalent diameter of the lead particles in the atmosphere will be approximately 0.25 microns. The mass of each nuclei will then be

$$M = 4/3\ \pi\ (1.2 \times 10^{-5})^3\ g$$
$$= 7.3 \times 10^{-15}\ g$$

The concentration of lead in such a droplet will be

$$\frac{7.3 \times 10^{-15}\ g}{3.36 \times 10^{-8}\ cm^3} = 2.15 \times 10^{-7}\ g/cm^3 = 0.215\ mg/l$$

Therefore, on this basis, 9.3% of the droplets must form around lead nuclei to produce a lead concentration of 0.02 mg/l in rainfall. If the mass median equivalent diameter of the lead nuclei is assumed to be near 0.40 microns as reported by Lee (1968), similar calculations show that only 2.3% of the droplets must form around lead nuclei to produce a lead concentration of 0.02 mg/l. These values are reasonable since it has been shown (Table 5-4) that 1.8% to 4% of the mass of airborne particulate matter near the surface is lead. At higher levels, the small lead particles should account for a higher percentage of the total particulate matter.

Washout and rainout processes can result in significant concentrations of lead in rainfall. The U. S. Public Health Service maximum permissible concentration for lead in drinking water is 0.05 mg/l (PHS Drinking Water Standards, 1962). The rainfall data show that, in urban areas, the maximum permissible concentration is often exceeded in rainfall, and in heavily polluted areas it may be exceeded by several hundred percent. However, the lead concentrations in most water supplies in the United States are significantly lower than the rainfall concentrations (Lazrus, 1965). The exchange and filtration mechanisms active in the soil appear to remove the lead pollutants effectively.

Rainfall and dry sedimentation are the major removal processes affecting lead particulate matter. Dry sedimentation accounted for 94% of the lead collected during the year at the freeway. Further from the heavily polluted freeway site the percentage of the lead removed by sedimentation decreased. The data suggest that in areas of California removed from heavy traffic, rainfall might account for 10% or more of the lead contamination reaching the ground. In areas with rainfall scattered throughout the entire year and receiving more annual precipitation than the 13 inches expected in Palo Alto, rainfall may account for a larger percentage of the lead contamination reaching the surface.

A third process by which pollutants are removed from the atmosphere is the impaction of particles on surfaces. During the rainfall season 92% more lead was deposited in a rainfall collector placed under a tree at the freeway than was deposited in rainfall and dry fallout collectors placed nearby in the open. The lead to non-volatile solids ratio in the drippings from the tree was lower than the ratio in the dry fallout. This may indicate a more efficient collection of the larger dust particles by the leaf surfaces or a more efficient removal of the larger dust particles from the leaf surface by rainfall. The percent of soluble lead in the drippings from the tree was much higher (27.7% compared to 6% in the dry fallout), perhaps due to the ability of the droplets forming around soluble nuclei to remain moist for longer periods of time. These droplets would be impacted and effectively held on the leaf surface while nuclei which impact as dry particles would be held more loosely and dislodged by air turbulence or lead motion to be reentrained in the airstream. On the other hand, the high soluble lead content of the drippings may result from preferential removal of the soluble lead particles from the leaf surface by rainfall. The reasons for this increased amount of soluble lead in the drippings are not obvious, and detailed experimentation and sampling is needed to fully understand the impaction process.

The field sampling data indicate that the proportion of lead pollutants removed rapidly from the atmosphere by dry sedimentation could be increased by changing the form of the alkyl lead combustion products from automobile engines. Lead pollutants exhausted in the form of particles which are more effective as condensation nuclei and which can retain moisture for a longer period of time should be removed more efficiently. A change in the types of scavengers added to the fuel could possibly produce more "desirable" pollutants. A rapid and more complete removal of lead pollutants would produce more severe contamination near heavily traveled roadways, but would result in less air pollution and surface contamination in areas removed from heavy traffic. Rainfall near the heavily traveled roadways would also contain higher concentrations of lead pollutants, but the rainfall in other areas would contain less lead.

The airborne lead concentrations observed at the freeway site would not be significantly affected by changing the form of the pollutants exhausted by automobiles. The amount of lead pollutants exhausted by each vehicle would have to be decreased to significantly reduce the high airborne lead concentrations which often exist near major roadways.

Laboratory Studies

The results of the field sampling portion of this study indicate that the nucleation of water droplets around lead aerosol particles is an important process contributing to the rapid removal of a large portion of the lead contaminants present in the atmosphere. The second phase of this study was undertaken to observe lead compound aerosol particles in a slightly supersaturated environment to learn more about the nucleation of water vapor on these particles, and the factors which determine the rate at which nucleation will take place.

The modified thermal gradient supersaturation chamber used in this program has proven to be a useful tool for studying the heterogeneous nucleation process. The results of the lead aerosol tests indicate that the processes in the chamber occur as anticipated, but some questions remain to be answered. For example, with no temperature gradient across the chamber ($\Delta T = 0$) no nucleation and aerosol removal should occur; but, the extrapolated curves presented in Chapter 5, Figures 5-21, 5-22, 5-23, and 5-24 show that the intercepts are all greater than zero and increase with aerosol particle size. Also, the convective currents and air flow mixing in the chamber may affect the initial degree of supersaturation reached in the chamber. The extent of this effect is not known, but it should be small. More instrumentation and testing is needed to answer these questions. However, since these unanswered questions remain, all the results from the nucleation tests have been reported in relative terms. The complexities of the chamber and the dynamic condensation and evaporation processes occurring make absolute rates very difficult to determine for the specific aerosols.

The data obtained from the thermal gradient supersaturation chamber tests show that, under similar conditions, aerosol particles of some lead compounds are much better condensation nuclei than others. The differences in the nucleation rates observed were significant enough to be easily detected. The data from the supersaturation chamber tests are summarized in Figures 6-2 and 6-3.

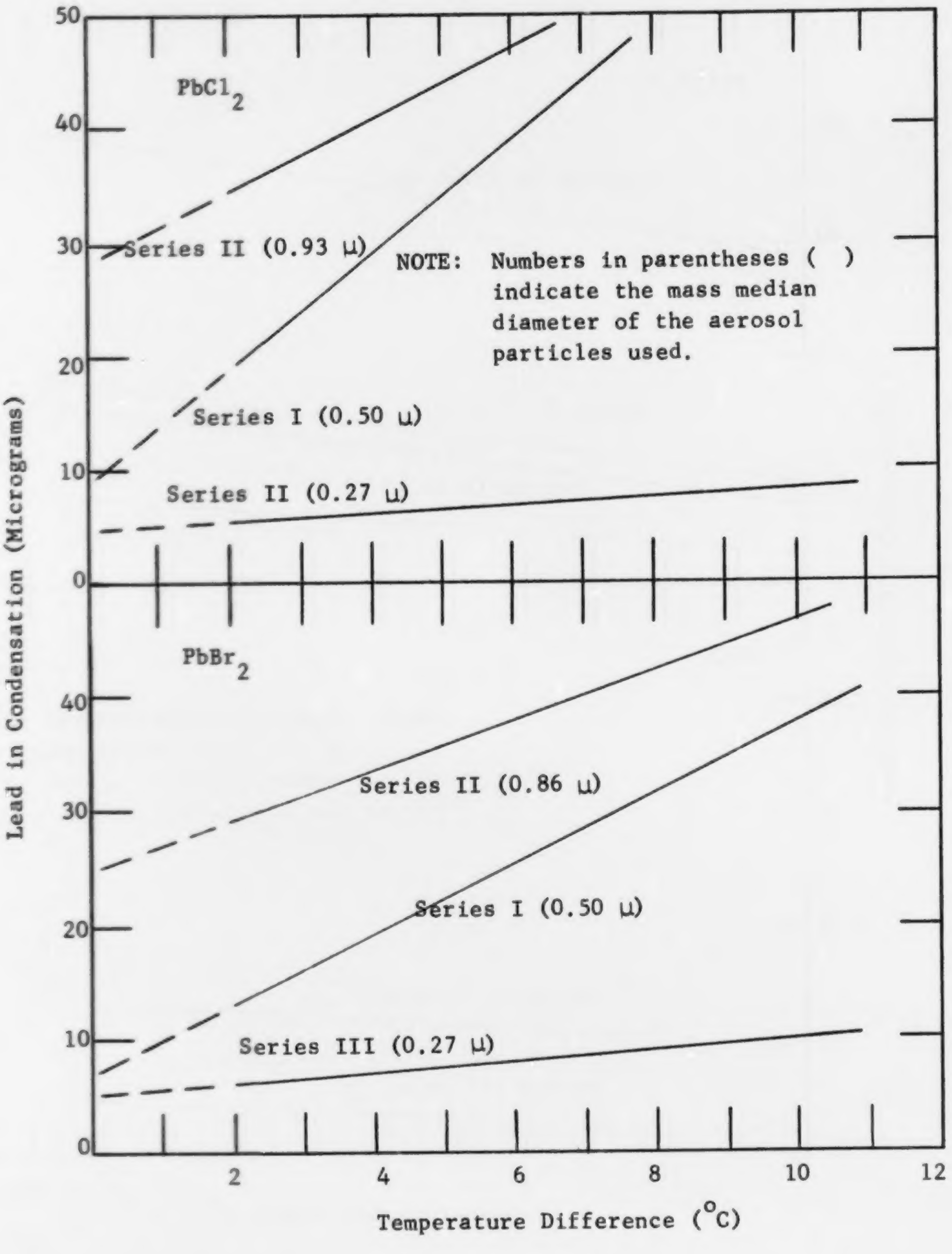


FIGURE 6-2
DIFFUSION CHAMBER RESULTS

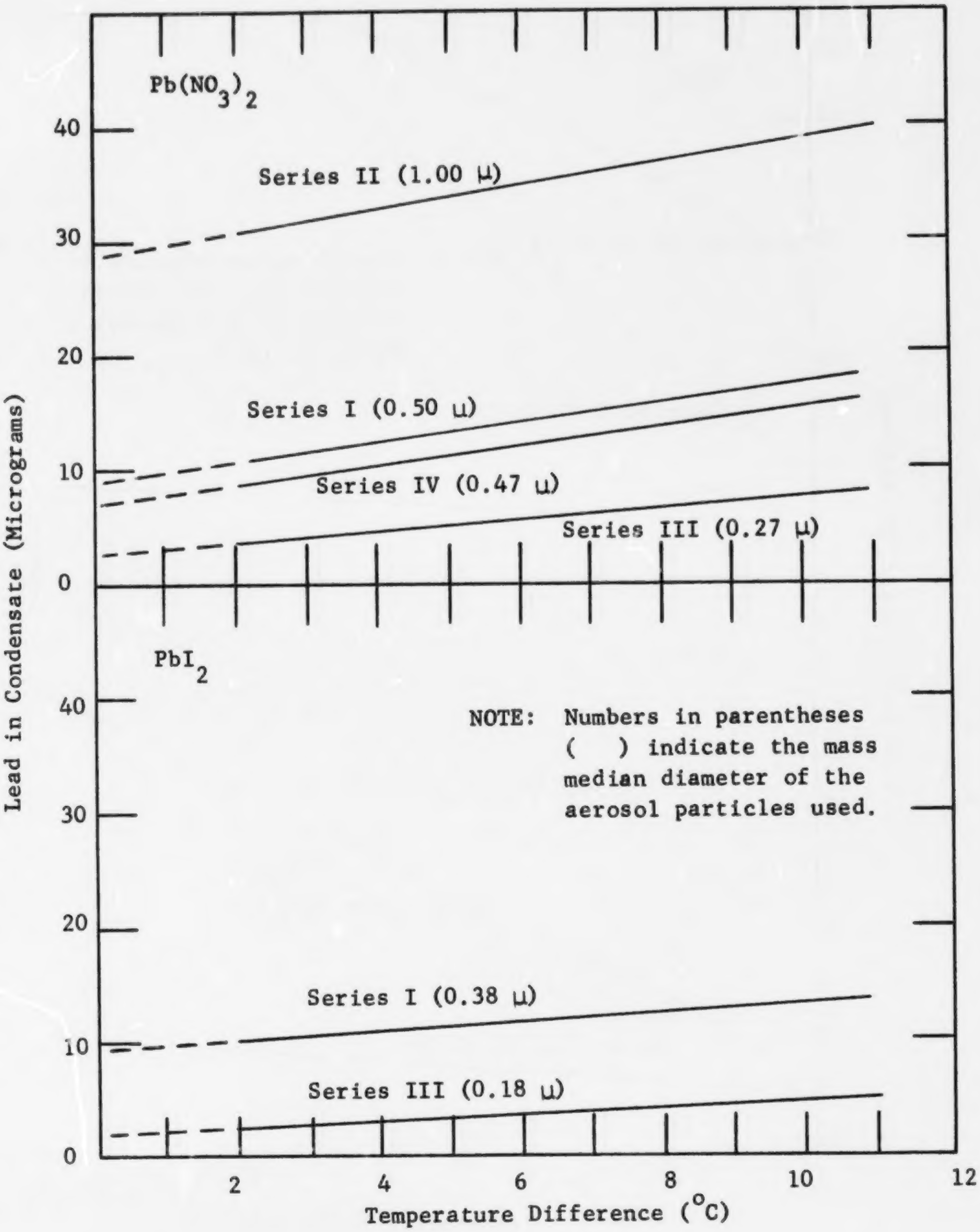


FIGURE 6-3
DIFFUSION CHAMBER RESULTS

The nucleation of droplets around aerosol particles did not occur as thermodynamic theory predicts. The larger, more soluble, particles did not necessarily make the best nuclei for condensation. PbI_2 aerosol particles, relatively insoluble and non-wettable, condensed water vapor rapidly, more rapidly than larger aerosol particles of more soluble compounds. $Pb(NO_3)_2$, an extremely soluble compound, condensed water more rapidly than $PbCl_2$ and $PbBr_2$ particles of the same size. When the average size of the aerosol particles was doubled, the nucleation rate for the $Pb(NO_3)_2$ particles remained the same, but the rate for $PbCl_2$ and $PbBr_2$ particles increased. This increase in the rate of nucleation may have occurred because the larger particles offered a much larger surface area where nucleation was initiated at several points simultaneously--producing a droplet more quickly. Evidently, this simultaneous nucleation did not occur on the very soluble $Pb(NO_3)_2$ particles. Any moisture which formed on the soluble, wettable surface of a $Pb(NO_3)_2$ particles tended to move more quickly over the entire surface rather than to form individual caps of moisture.

The most surprising result of these tests is that the very small particles near the Aitken range acted rapidly as condensation nuclei, more rapidly than the larger particles tested. The rate of nucleation for these small particles appears to be independent of the type of lead compound making up the aerosol particles. More experimentation and study will be needed to explain this unexpected result. This rapid nucleation on small particles may have been overlooked in the past because few of the droplets thus formed will continue to grow. These water droplets will be very small initially, and will have a large degree of curvature. Kelvin's equation predicts that this large degree of curvature will result in a high vapor pressure over the droplet surface, discouraging further growth by condensation. Therefore, in a naturally occurring mixed nuclei population, the Aitken particles may act as condensation nuclei, but few of the droplets formed will grow large in the presence of droplets which initiated around large nuclei.

The tests conducted in this program indicate that the nucleation of water droplets on small particles may be similar to a rapid chemical reaction with the particles acting as catalysts. It appears to be much different from the relatively slow nucleation of water on a plane surface. Parameters such as solubility, wettability, and particle size do not seem to be as important as previously thought in determining how well submicronic particles will act as condensation nuclei.

Since nucleation is a surface reaction occurring at the nuclei-vapor interface, the surface energy, the surface structure, and the surface forces of attraction and repulsion should be of importance. These parameters will determine, in part at least, the ability of the potential nucleus to attract and hold water vapor molecules closely enough to produce a stable droplet. A large number of vapor molecules undergoing the phase change from vapor to liquid are required to overcome the free energy barrier which prevents spontaneous nucleation in a supersaturated system.

The surface free energy of a solid nucleus is extremely difficult to measure, but the crystalline structure of the nuclei particles is known. The PbI_2 particles, which are hexagonal crystals very similar to ice crystals, seem to be the best nuclei. $Pb(NO_3)_2$ particles, which are cubical crystals similar to $NaCl$ crystals, are also good nuclei. $PbBr_2$ and $PbCl_2$ particles, which are rhombic or monoclinic crystals, are poorer condensation nuclei. This suggests that the more nearly a crystal resembles ice crystals, the better it will be as a condensation nucleus. These various crystals form as a result of the attractive and repulsive forces acting upon the atoms forming the compounds. Perhaps these forces extend beyond the crystal surface and affect the water vapor molecules nearby. The surface forces of the PbI_2 crystals may result in better orientation and packing of the vapor molecules with minimum energy losses, allowing the phase change from the gaseous to the liquid state to occur more rapidly.

There are many other reasons that may account for the different nucleation rates observed in this study, including surface impurities on the nuclei, surface defects on the crystal surfaces, energy losses at the interface, absorption and adsorption of vapor molecules and others. This work was undertaken as an exploratory study to develop equipment and techniques to observe the nucleation rates on four specific compounds of interest. Further tests with various other compounds are needed to evaluate the effect of various chemical and physical parameters on the rate at which nucleation occurs.

CHAPTER SEVEN

CONCLUSIONS

In summary, the work completed in this study can be used as a basis for the following conclusions:

1. The thermal gradient diffusion chamber has proven to be a useful tool to study the nucleation of water droplets on aerosol particles.
2. The solubility, wettability, and size of the aerosol particles are not as important as previously suspected in determining how well a particle will serve as a condensation nucleus.
3. The crystalline structure of an aerosol particle seems to be important in determining how the particle will react in a supersaturated environment. Nucleation occurs more rapidly on particles with a crystalline structure similar to ice.
4. Nucleation occurs rapidly on very small particles near the Aitken range, but few large droplets will be produced by such small nuclei in a mixed aerosol system. The large degree of curvature exhibited by the small droplets produced initially increases the saturation vapor pressure over the droplet surface and will discourage further growth by condensation.

5. Lead compound particles act as condensation nuclei in slightly supersaturated systems, even if the particles are extremely small and relatively insoluble.

6. Nucleation occurs at a rapid rate on PbI_2 and $Pb(NO_3)_2$ particles, and more slowly on $PbBr_2$ and $PbCl_2$ particles.

7. Dry fallout contains significant quantities of lead, especially fallout collected near a heavily traveled freeway. The results of this study indicate that the nucleation and condensation of water vapor on the submicronic-sized lead particles contained in automobile exhaust could account for the removal of lead pollutants by sedimentation.

8. Dry sedimentation and rainfall are the major processes by which lead pollutants are removed from the atmosphere. In a heavily polluted area, rainfall may account for a few percent of the total amount removed each year, but in areas removed from major roadways, sedimentation becomes less effective and rainfall may account for 10% or more of the lead removal.

9. The impaction of particulate matter on leaf surfaces increases the amount of lead removed from the atmosphere. The drippings from tree leaves during the rainy season contained 92% more lead pollutants than the rainfall and dry fallout collected nearby in an open area.

10. Lead compound particles which are good condensation nuclei and can retain moisture for long periods of time should be removed from the atmosphere more effectively than lead particles which are not good nuclei.

CHAPTER EIGHT

SUGGESTIONS FOR FUTURE WORK

Scientific investigations are seldom ends in themselves. They are merely steps toward a fuller understanding of the problem studied. Such is the case with the program reported here. The results obtained during this study suggest that future work conducted in the following areas may produce interesting and useful results:

-- Extensive and more complete sampling should be conducted in the Palo Alto area to further study the lead removal processes active in an urban environment. A grid of 12 to 15 sampling sites in this area would yield more detailed information concerning the movement of lead pollutants in a suburban area and the effectiveness of the natural cleansing processes in removing pollutants.

-- The impaction of particulate matter on leaf surfaces and its subsequent removal by rainfall should be studied in more detail. Continuous field sampling of rainfall and fallout should be conducted in open areas and under trees. Laboratory tests to determine the amount of lead pollutants on individual leaves and to observe how easily these pollutants are removed by rinsing would be useful.

-- The condensation nuclei chamber should be used for further studies on lead aerosols and other aerosol particles of interest. The results of such studies could be used to estimate which parameters are most important in determining how well particles will act as nuclei. Neutron activation analysis, atomic absorption and other sensitive analytic techniques could be used to analyze the collected condensate.

-- Aerosol tests should be conducted using mixed aerosol populations to study the effects of different types of nuclei (e.g. $PbCl_2$ and NaCl) on one another in a slightly supersaturated atmosphere.

-- A device capable of rapidly measuring the degree of supersaturation in the condensation nuclei chamber (perhaps similar to the device developed by Barrows (1965) should be installed in the chamber to observe the changes in the degree of supersaturation which may occur in a growing cloud.

-- Extensive studies should be conducted on small particles near the Aitken range to determine why the rate of nucleation appears to be independent of the chemical composition of the particles.

APPENDIX A

AIR SAMPLE DATA
(Figures 5-1 through 5-7)

Freeway Site

Time	Traffic Flow Vehicles/minute	Lead Concentration ($\mu g/m^3$)	Wind Speed mph	Comments
		August 15, 1966		
0500	7	2.5		
0530	20	1.1		
0600	41	1.9		
0700	135	6.5		
0745	162	14.2		CLEAR
0900	73	8.7		
1000	78	5.3		
1100	82	9.6		AND
1200	88	9.2		
1300	88	8.7	8	
1400	88	8.2	9	WARM
1500	98	11.0	10	
1600	157	10.6	12	
1700	147	7.0	14	
1800	98	6.8	10	
1900	81	2.8	8	
		September 12, 1966		
0500	8	2.5		
0600	33	5.9		
0700	129	2.9		
0730	175	5.9		
0800	143	6.2		CLEAR
0900	108	11.6		
1000	85	12.2		
1100	82	9.8	3	AND
1200	90	6.9	9	
1300	77	5.8	6	
1400	86	4.3	5	WARM
1500	102	9.2	9	
1600	148	12.6	11	
1700	159	8.5	9	
1800	125	3.5	10	

APPENDIX A, Continued

Freeway Site

Time	Traffic Flow Vehicles/minute	Lead Concentration ($\mu g/m^3$)	Wind Speed mph	Comments
September 30, 1966				
0530	21	1.0	2	
0600	72	1.0	3	
0645	116	4.4		
0745	181	8.9	3	HAZY
0845	110	17.6	2	
0945	75	14.6	6	
1045	77	8.5	4	
1145	92	8.0	5	AND
1245	84	12.2	9	
1345	84	6.6	12	
1445	101	6.2	15	WARM
1545	166	10.2	16	
1645	145	9.8	12	
1745	128	6.9	11	
November 3, 1966				
0445	7	3.6		
0545	10	2.5		
0645	123	5.1		
0745	193	18.2		
0845	123	11.0		HAZY
0945	104	10.0	6	
1045	80	7.3	4	
1145	94	7.7	6	AND
1245	86	6.1	8	
1345	85	9.5	5	
1445	87	10.7	8	
1545	128	8.5	7	COOL
1645	165	6.0	8	
1745	125	6.5	3	

APPENDIX A, Continued

Freeway Site

Time	Traffic Flow Vehicles/minute	Lead Concentration ($\mu g/m^3$)	Wind Speed mph	Comments
		December 6, 1966		
0515	5	2.2	LIGHT WIND	MODERATE RAIN
0615	51	1.6		
0715	128	2.3		
0815	138	5.3		
0915	75	4.1		
		March 16, 1967		
0500	6	3.1	WINDY	LIGHT RAIN
0600	33	3.7		
0630	88	7.4		
0700	119	4.5		
0800	140	2.2		
0900	121	5.1		
1000	95	4.3		
		March 31, 1967		
0515	12	1.7	LIGHT WIND	MODERATE RAIN
0615	42	1.9		
0645	100	4.9		
0715	147	2.9		
		April 6, 1967		
0630	118	1.0	NO WIND	MODERATE RAIN
0700	129	2.9		
0745	160	2.4		
0915	92	5.5		
		April 14, 1967		
0600	26	1.4	LIGHT WIND	COOL AND CLEAR
0645	130	0.3		
0730	172	1.4		
0815	155	0.8		
0910	75	4.2		
0945	85	5.5	WINDY	

APPENDIX A, Continued

Freeway Site

Time	Traffic Flow Vehicles/minute	Lead Concentration (μg/m^3)	Wind Speed mph	Comments
April 20, 1967				
0600	25	1.2	WINDY	COOL AND CLEAR
0645	115	5.6		
0745	107	9.3		
0845	120	8.2		
0950	90	6.8		
August 1, 1967				
0545	35	4.8	NO WIND	CLEAR AND WARM
0615	75	6.2		
0645	95	10.5		
0715	160	12.4		
0755	148	10.0		
0820	154	11.7		
0905	95	6.7		
1005	95	6.4		
September 19, 1967				
0530	10	2.4	LIGHT WIND	HAZY AND WARM
0600	29	2.3		
0630	80	4.0		
0700	138	5.2		
0730	170	4.6		
0800	145	9.8		
0830	122	7.9		
0900	114	8.1		
1000	88	6.9		

APPENDIX A, Continued

All Three Sites

Freeway			Residential		Foothills	
Time	Traffic Flow (Veh/min)	Lead Conc. ($\mu g/m^3$)	Time	Lead Conc. ($\mu g/m^3$)	Time	Lead Conc. ($\mu g/m^3$)
September 1, 1967						
0700	70	8.15	0600	2.85	0800	1.50
0730	193	12.60	0700	4.73	0945	4.15
0840	95	14.70	0800	5.11	1145	3.20
0940	73	12.50	0900	3.95	1400	2.95
1100	79	8.30	1000	3.95	1700	2.90
1330	71	7.20	1315	3.80		
1600	140	9.00	1530	4.10		
1715	169	6.10	1730	3.35		
November 1, 1967						
			0830	3.00	0900	2.20
			0930	3.20	1000	1.50
			1030	2.70	1100	1.90
November 7, 1967						
0615	70	3.48	0630	1.60	0805	5.10
0700	150	5.90	0740	2.50	0945	3.50
0745	194	10.0	0850	4.6	1045	4.3
0830	110	8.9	1000	4.6	1345	3.6
0915	71	19.0	1115	3.9	1630	3.9
1015	72	13.0	1530	4.1		
1330	83	7.2	1730	4.3		
1600	157	9.0				
1715	183	6.1				

APPENDIX B

LEAST SQUARES ANALYSIS

(FROM: ENGINEERING STATISTICS, Albert H. Bowker, Gerald J. Lieberman, Prentice Hall, Inc., Englewood Cliffs, New Jersey, 1959).

Sample Calculation--Series III Chamber Data, $PbCl_2$

x	y	x^2	y^2	xy
3.0	2.7	9.00	7.29	8.1
3.5	6.0	12.25	36.00	21.0
4.0	5.2	16.00	27.40	20.8
5.5	5.5	30.25	30.25	30.25
7.0	3.7	49.00	13.70	25.9
7.0	8.0	49.00	64.00	56.0
7.5	6.7	56.25	44.90	50.3
7.5	7.2	56.25	51.94	54.0
7.5	8.4	56.25	70.26	63.0
7.5	8.9	56.25	79.11	66.7
8.0	7.2	64.00	51.94	57.6
8.5	7.4	72.25	54.86	62.9
8.5	9.2	72.25	84.64	73.2
78.0	86.1	599.00	616.29	589.75

Assume Relationship $y = a + bx$

x represents temperature difference between chamber surfaces:

$\Sigma x_i = 780$; $\bar{x} = \Sigma x_i/n = 6.0$; $(\Sigma x_i)\bar{x} = 468$;

$\Sigma x_i^2 = 599$;

$\Sigma x_i^2 - (\Sigma x_i)\bar{x} = \Sigma(x_i - \bar{x})^2 = 131.$

y represents lead collected in chamber:

$\Sigma y_i = 86.1$; $\bar{y} = \Sigma y_i/n = 6.62$; $(\Sigma y_i)\bar{y} = 569.0$;

$\Sigma y_i^2 = 616.3$; $\Sigma y_i^2 - (\Sigma y_i)\bar{y} = \Sigma(y_i - \bar{y})^2 = 47.3$.

$n = 13$; $1/n = .077$; $(\Sigma x_i)(\Sigma y_i)/n = \bar{x}\ \Sigma y_i = 516.6$;

$\Sigma x_i y_i = 589.7$;

$\Sigma x_i y_i - (\Sigma x_i)(\Sigma y_i)/n = \Sigma(x_i - \bar{x})(y_i - \bar{y}) = 73.1$

$[\Sigma(x_i - \bar{x})(y_i - \bar{y})]^2 = 5350$;

$$\frac{[\Sigma(x_i - \bar{x})(y_i - \bar{y})]^2}{\Sigma(x_i - \bar{x})^2} = 40.8.$$

DATA FOR EQUATION OF LINE:

$$b = \frac{\Sigma(x_i - \bar{x})(y_i - \bar{y})}{\Sigma(x_i - \bar{x})^2} = 0.56; \quad a = \bar{y} - b\bar{x} = 3.30;$$

equation of line = $y = a + bx = 3.30 + 0.56\ x$.

ESTIMATION OF STANDARD DEVIATION:

$$(n - 2)s^2_{y/x} = \Sigma(y_i - \bar{y})^2 - \frac{[\Sigma(x_i - \bar{x})(y_i - \bar{y})]^2}{\Sigma(x_i - \bar{x})^2} = 6.5;$$

$s^2_{y/x} = 0.59$; $s_{y/x} = 0.77$.

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